A STUDY OF THE FACTORS INFLUENCING THE LIFE CYCLE OF SYNTHETIC ANION EXCHANGE RESINS, WITH SPECIAL REFERENCE TO THE EXTRACTION OF URANIUM

A

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by

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Thesis

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I N D E X (Continued)

VITAE CURRICULUM

1) B.Sc. (Eng.) Rand. Cum Laude. March 1951

2) Employed as Metallurgical Assistant at the Government Metallurgical Laboratory, Milner Park, Johannesburg. Undertook Research work on the Extraction of Uranium from the Rand Ores. December 1950

3) The following Secret Reports were Submitted during the period of the Investigation included in this thesis.

Government Metallurgical Laboratory. Progress Reports (Leaching)

(a) No. 45 "Report on the Life of Anion Exchange Resins Amberlite & Dowex." May 1951

(b) No. 47 "Capacity Tests on Amberlite & Dowex Resins." May 1951

(c) No. 58 "Report on the Life of Anion Exchange Resins Amberlite & Dowex No. (2) 200 cycles." July 1951

(d) No. 63 "Regeneration Tests on a Sample of Poisoned Amberlite IRA 400 Ion Exchange Resin from Western Reefs Pilot Plant." (Dr. N.G. Atmore & R.E. Robinson) Aug. 1951

(e) No. 68 "Further Regeneration Tests on Samples of Poisoned Amberlite IRA 400 Anion Exchange Resins from Western Reefs and Blyvooruitzicht Pilot Plants." (Dr. N.G. Atmore & R.E. Robinson) Oct. 1951

(f) No. 81 "Report on the Poisoning of Western Reefs Resin." Jan. 1952

(g) No. 91 "Report on the Life of Amberlite IRA 400 and Dowex I Anion Exchange Resins No.(3) Results after 600 cycles." May 1952

(h) No.107 "The Nature of the poisons occurring on the Western Reefs Anion Exchange Resins." Sept. 1952

(i) No.115 "Report on the Cobalticyanide Poisoning of West Rand Consolidated Ion Exchange Resins." Feb. 1953

(j) No.127 "Further Investigations into the Poisoning at West Rand Consolidated Uranium Plant." March 1953

(k) No.133 "Factors Influencing the formation of Polythionates during the Uranium Leach." April 1953

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(l) No.151 "Final report on the Life-Test of Amberlite IRA 400, Dowex I, Permutit and Ionac Resins using Blyvooruitzicht Pregnant Solutions." July 195

Government Metallurgical Laboratory. Progress Reports (Analytical)

(m) "The Analysis of Eluting and Pregnant Solutions for Cobalti-cyanide $[Co(CN)_6]'''$ May 195

GENERAL SUMMARY

Investigations have been carried out into the life of various Anion Exchange Resins employed on the Rand for the extraction of uranium from the uranium Leach Liquors.

It was found that in the case of the leach liquors produced at the Western Reefs Pilot Plant, and at the West Rand Consolidated Uranium plant, the major factor causing a decrease in the efficiency of the Ion exchange resins was the presence of certain chemical poisons in these pregnant solutions. These poisons were identified as the Cobalticyanide Anion $Co(CN)_6'''$ and the Tetrathionate anion S_4O_6''. Both these compounds are derived from cyanidation of the ore for gold extraction prior to the uranium leach. The cobalticyanide is formed during the cyanidation, and also in certain cases during the addition of a recycled Manganese Dioxide slurry containing cobalt to the slightly alkaline cyanide residue, containing traces of cyanide anions. The tetrathionate is formed by the oxidation of thiocyanate anions, formed during cyanidation, by the acid oxidizing conditions obtained in the uranium leach. The amount of these compounds appearing in the pregnant solutions can be considerably reduced by the thorough washing of the cyanide residue prior to the uranium leach.

Of these two chemical poisons, the cobalticyanide anion is the most serious. Although generally present in smaller concentrations than the tetrathionate anions, it is strongly adsorbed by the resin, and once adsorbed is

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extremely difficult to remove. It therefore constitutes a serious cumulative poison. The tetrathionate anion on the other hand, although strongly adsorbed, is partially removed by the acid nitrate eluting solution, and can also be completely removed by regeneration procedures such as treating the poisoned resin with 30% NaOH or 5% Na_2S. A method was developed for the removal of cobalticyanide from the poisoned resins by means of hot 50% NH_4CNS, but this was not economic on a large scale. Therefore several alternative methods were discussed with a view to the elimination of the cobalticyanide anions before coming into contact with the ion exchange columns.

Experiments were also conducted on the life of various resins operating on pregnant solutions produced at the Blyvooruitzicht Pilot Plant.

In these solutions the amounts of the poisons were very small and did not constitute a major consideration in the life of the resins. In this case a detailed study was made of the resin losses likely to occur due to the disintegration and subsequent removal of the fine resin particles during the backwashing operations. It was found that by taking certain precautions, these losses could be reduced to a minimum, so that no special consideration need be devoted to the production of a resin with an exceptionally high abrasion resistance.

INTRODUCTION

INTRODUCTION

The use of synthetic organic anion exchange resins provided an efficient and economic method of isolating uranium from the Rand leach liquors. This particular application of ion exchange was unusual in that these resins were used not only to obtain a uranium concentrate from fairly dilute solutions but also to separate the uranium from a relatively large concentration of impurities arising from the acid leaching of the Rand Cyanide residues.

Because of this wide variety of compounds occurring in the leach liquors, it was initially appreciated that a strong possibility existed that these ion exchange resins would eventually become poisoned and unsuitable for further use.

One of the major expenses involved in the separation of uranium by means of anion exchange was the high initial cost of the exchange resins. It was therefore apparent that the longer the useful life of these resins, the lower would be the production costs per lb. of uranium.

An investigation was thus considered necessary into the ways whereby the life of these resins might be decreased, either by poisoning, physical disintegration or any other means, and also what provision should be made to ensure as long a resin life as possible.

At the same time a comparative study of the different anion exchange resins then available would be of great value in ensuring that the most suitable resin as regards stability, capacity and resistance to poisoning should be chosen for the full scale operation of the uranium extraction plants.

The large scale use of the ion exchange process introduced into South Africa a new technique about which only the

fundamentals.....

fundamentals were understood. It was important, therefore, to correlate the vast amount of work that had been done in other countries on other applications with the specific problem of extracting uranium from the Rand leach liquors. To this end a system of standard tests was necessary for the evaluation of the suitability of the various anion exchange resins for the extraction of uranium.

SCOPE OF THE INVESTIGATION

SECTION A. A Study of the Poisoning Occurring on the Western Reefs Pilot Plant and the West Rand Consolidated Anion Exchange Resisn, Amberlite IRA.400.

Investigations were carried out on samples of poisoned Amberlite IRA.400 resin from the Western Reefs Pilot Plant. These resins had become poisoned almost immediately after being put into operation. Later it was found that the resin from the West Rand Consolidated Uranium Plant suffered from the same type of poisoning and the techniques developed for Western Reefs were applied in the case of the latter resins.

The investigations covered the following field:-

(a) Methods of regenerating the poisoned resin.

(b) A fundamental study of the nature of the poisons.

(c) The methods whereby the poisons are introduced into the pregnant solutions.

(d) A detailed study of the factors influencing the formation of the poisons at the West Rand Consolidated Plant.

(e) Preliminary tests on the elimination of the poisons, and the discussion on the various methods being studied by other investigators.

SECTION B. Investigations into the Life of Various Resins Operating on Blyvooruitzicht Pregnant Solutions.

Investigations were carried out on the life of, initially, Amberlite IRA.400 and Dowex I resins, and later also Ionac SE and Permutit SE resins on Blyvooruitzicht Pregnant Solutions.

The investigations were commenced on solutions obtained from the Pilot Plant, but later it was found necessary to produce these solutions at the Government Metallurgical

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Laboratory under standard conditions to provide comparable results.

The investigations covered the following field:-

(a) A study of the mechanical losses of resin occurring during Uranium extraction operations.

(b) A study of the factors influencing the disintegration of the various resins during column operation.

(c) A study of the chemical poisoning occurring on resins operating on Blyvooruitzicht Pregnant Solutions.

(d) A brief comparison of the suitability of the various resins under life test.

SECTION C. Standard Tests and Analytical Methods.

During the course of the investigation, it was necessary to develop certain standard tests and analytical methods whereby the properties of the various fresh and poisoned resins could be assessed.

The standard tests and analytical methods developed were as follows:-

(a) Uranium capacity and chloride capacity tests.

A standard test was developed whereby the actual capacity of the resins for extracting uranium could be measured. This test was necessary to replace the capacity tests using pregnant solutions used by earlier investigators, since the capacity of the resins using these solutions was subject to too many variables, the significance of which was not fully understood understood.

(b) Analyses of the resins for total nitrogen, ash, silica, total sulphur, cobalt, iron, uranium, and certain other non-volatile elements.

These methods were merely adapted from standard analytical procedures to apply to resin analyses.

(c) a.....

(c) A method of analysis for tetrathionates on anion exchange resins.

No method was previously available for determining the amount of this poison on the resins. A new method was developed during the course of the investigation into the nature of the poisons and adapted for analytical use.

(d) A colourimetric method of analysis for tetrathionate in pregnant and eluting solutions.

No method was available for the determination of trace amounts of tetrathionate in the presence of large amounts of SO_4'', Fe^{+++} and other impurities. A colourimetric method was developed, and the effect of certain variables in the experimental procedure studied.

(e) Analysis of plant solutions for traces of cobalticyanide anion.

A sensitive colourimetric method for the determination of cobalt was available and was adapted to the determination of cobalticyanide anions from cationic cobalt and other interfering elements.

The standard tests and analytical methods were investigated only as far as was necessary to ensure that adequate and reproducible results were obtained of sufficient accuracy to satisfy the requirements of the investigations on hand.

HISTORICAL REVIEW

The literature contains a vast amount of reported work on ion exchange, and only that directly connected with this thesis will be included in this review. The reported work is considered in two sections. The first includes experiments undertaken at the Massachusetts Institute of Technology in America, and the Chemical Research Laboratory, Teddington, England, which were directed specifically towards the extraction of Uranium from Rand Leach Liquors, and described in a series of secret reports.

The second includes a Review of Articles appearing in the periodical literature which contains information pertaining to the work carried out in this investigation.

PREVIOUS WORK CARRIED OUT AT THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY AND THE CHEMICAL RESEARCH LABORATORY, TEDDINGTON.

In a report issued in August 1949, N.N. Schiff[119] describes attempts to isolate Uranium from Rand Leach Liquors using the Cation exchange resin Nalcite HCR. These attempts were unsuccessful, a concentration of all the cations except silica being obtained.

Later both the Dow Chemical Laboratory and the Batelle Memorial Institute showed that Uranyl Uranium is capable of being adsorbed on anion exchange resins from solutions containing either sulphates or phosphates as complex uranyl sulphate or phosphate anions.

N.N. Schiff,[120] acting on these suggestions, undertook experiments on the sulphuric acid leach liquors obtained on the Rand, using the anion exchange resins Dowex I, Dowex II, and Amberlite IRA.400. Schiff showed that by using a single

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column of Dowex I, as much as 97% of the Uranium present in the leach liquors could be isolated in a reasonably pure form. We also found that the capacities for Uranium of the three resins studied were as follows:-

	Capacity in Mgms. U_3O_8/g resin	
	+ 28 mesh	- 28 mesh
Amberlite IRA.400	45	46
Dowex I	43	45
Dowex II	41	42

Amberlite IRA.400 was observed to have the highest reaction rate.

The use of an acid eluting solution (namely 0.9N NaCl and 0.1N HCl) was reported to be effective in removing the adsorbed uranium from the anion exchange resin.

A marked difference was observed in the effieiency of this ion exchange process operating on the two types of pregnant solutions produced at that time. In the case of the "X" leach liquor (at a pH of approximately 1.5) about five times as much resin is required as in the case of the "Y" leach liquor (where a large portion of the excess acid was neutralized with lime, bringing the solution to a pH of 3.0).

An approximate cost estimate was given, based on a single column operating on a Blyvooruitzicht pregnant solution; treating 4,000 tons of ore a day and assuming a resin life of 1,000 cycles.

		Cost in $/lb. U_3O_8
(1) Resin	375 ft.^{3} @$70/ft.^{3} 26,250	0.05
(2) NaCl	5,75 lbs/ton ore @ $1.1/cwt.	0.16
(3) HCl		0.04
(4) NH_3		0.04
Total cost of resin and reagents		0.29

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This represented a maximum cost and it was realised that there were many means whereby the above figure could be substantially reduced. Nevertheless this process provided the most economic means of isolating the uranium found to date. The author based his estimate of the resin's life on the experience of the manufacturers, who claimed that the Dowex I resin, after testing with 27°Bé phosphoric acid for 1,000 cycles showed no serious decrease in capacity.

In a later report by S. Bailey,[121] and in a third report by M.M. Schiff,[125] methods whereby the above process might be improved by the use of three columns of resin in series, and the possibility of re-cycling the eluting solution reagents, were investigated. It was shown that much less resin was required in the three column system and that no difficulty was immediately apparent in re-cycling the eluting reagents, thus substantially reducing the cost of this process.
R.L. Barnard,[122] and later G.W. Lower,[128] in reports dealing with the fundamental reactions taking place, showed that the adsorbtion of uranium on Amberlite IRA.400 could be represented by the following reaction:-

$$(x - 1)\ R_2SO_4 + UO_2SO_4 \rightleftharpoons R_{2x-2}\left\{UO_2(SO_4)x\right\}$$

Where R- represents the active group on the anion exchange resin. By measuring the amount of sulphate and uranium in the eluates, the following ratios were obtained:-

$$\frac{\text{mols } SO_4''}{\text{mols U}} = 2.9$$

and $$\frac{\text{molar capacity of resin for Cl}}{\text{molar capacity of resin for U}} = 4.4$$

suggesting that the formula of the uranyl complex was $\left\{UO_2(SO_4)_3\right\}^{4-}$.

In these excellent reports a considerable amount of work was described on the measurement of the Chloride capacity

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and the Uranium capacity of the resin (Amberlite IRA.400) which formed the basis of the standard tests given in this Thesis.

F.N. Oberg[134] investigated the feasibility of introducing the resin into the acid pulp before filtration. The conclusion reached was that there existed a distinct possibility of eliminating filtration by this procedure. However the most important part of this report is the comparison between the different types of resin and the effect of certain variables on the adsorbtion of Uranium. The resins studied were Dowex I, Dowex II, Amberlite IRA.400, Amberlite XE.98, Permutit XAX, Amberlite IR4B, Deacidite E (British), Deacidite (U.S.A.), Permutit S, Amberlite 410 and Ionac 300. It was found that as regards rate of reaction and capacity, the Amberlite IRA.400 resin surpassed any of the others.

In addition Oberg studied the following variables influencing the adsorbtion of uranium.

(a) The effect of particle size, where it was found that the smaller the particles, the higher the rate of adsorbtion.

(b) The effect of the percentage crosslinking of the resin, where it was found that the higher the crosslinking, the greater the amount of uranium adsorbed and the faster the reaction rate.

(c) The effect of the pH and ferric ion concentration in the Leach Liquors on the adsorbtion of Uranium.

Oberg claimed that it was the higher pH of the "Y" process leach liquor and not the lower ferric ion concentration that was responsible for its superior adsorbtion properties compared with the "X" process leach liquor.

Further studies by N.V. Schiff[127] on the three column adsorbtion procedure, enabled him to arrive at a more accurate estimate of the cost of extracting uranium from the Rand cyanide residues.

The reagent consumptions given below are based on a plant

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treating 4,000 tons of ore a day and a recovery of 0.4 lbs U_3O_8/ ton ore. The assumed reagents costs are;-

Resin	-	$ 63/cu. Ft.
HCl	-	$ 24/ ton
NH_3	-	$ 80/ ton
H_2SO_4	-	$ 10/ ton
MnO_2	-	$ 80/ ton
$CaCO_3$	-	$ 6/ ton

Complete resin replacement is assumed at one year's operation of 1,000 cycles in the case of the "Y" leach liquor, and half a year or 1,000 cycles in the case of the "X" leach liquor.

	"Y" Leach Liquor		"X" Leach Liquor	
	lbs/ton ore	$/lb U_3O_8	lbs/ton ore	$/lb U_3O_8
H_2SO_4	55	0.69	48	0.60
MnO_2	10	1.00	8.5	0.85
$CaCO_3$	25	0.19	0	0
HCl	0.55	0.05	2.5	0.23
NH_3	0.30	0.03	1.3	0.13
Resin.	400 cu ft.	0.05	800	0.18
		2.01		1.99

From these figures it was apparent that there was essentially no difference between the two processes from an economic point of view.

In a further report, V.N. Schiff[126] investigated the possibility of using anion exchange resins subsequent to counter-current decantation and showed that this method was just as effective in extracting the uranium from these solutions.

Further studies[127] on the "X" process leach liquor indicated that the optimum pH of the pregnant solution to be 1.4, which is contrary to F. Oberg's assertion that it is this low pH which is responsible for the inferior loading properties of these solutions.

During these latter investigations it was found that the

efficiency of the resin had rapidly deteriorated. The adsorbtion of Uranium from the solutions had dropped from 93% to 55% in 24 cycles. A 6N HCl wash increased the adsorbtion to only 84% which rapidly dropped again to 70%. No attempt was made to determine the reason for this drop in capacity, and analyses of the poisoned resin failed to show the presence of any particular impurity.

In an English report by T.D. Harbutt and G.L. Milward,[129] a similar series of tests to those reviewed above, are described. A synthetic pregnant solution was used for these tests and very similar results were obtained.

The most comprehensive series of reports on the use of ion exchange resins on the Rand leach liquors are those discribing work done by T.V. Arden, R.S. Olsen, J.J. Brunner and R.D. McDonald[133,140,141] on the design and operation of ion exchange columns at the Western Reefs and Blyvooruitzicht Pilot Plants.

The last of these reports by R.S. Olsen[133] goes into full detail of the operational procedure, reagent requirements, design calculations and the effect of recycling eluting solutions at the Western Reefs Pilot Plant. In addition a short series of tests on a simulated West Rand Consolidated pregnant solution was carried out. This report, which is used as a standard reference on the operation of the ion exchange columns, can be considered to represent a detailed description of the manner in which ion exchange will be used on the large scale uranium plants.

An excellent summary of all the work carried out at the Massachusetts Institute of Technology up to the 1st August 1950 is given in a report by R.D. McDonald, J.J. Brunner, J. Dasher and D. Kaufman[123]. This summary includes an analysis of the cost of producing uranium by means of anion exchange which is probably the most reliable obtained at this stage.

7/ Item....

	Item	£/month	shillings/lb. U_3O_8.
	Labor	1,854	0.89
	Supplies	1,044	0.49
Reagents	Resin	1,100	0.52
	NH_3	2,250	1.07
	HCl	1,500	0.72
Overhead Amortization of Plant			
Total Capital Cost (including interest)			
	£201,240	1,675	0.80
			4.4

However, the work of Olsen[133] has shown that the reagent costs (excluding the resin) can be cut down still further, as in the case of the Western Reefs Plant to 0.74 shillings/lb. U_3O_8.

REVIEW OF THE PERIODICAL LITERATURE ON ION EXCHANGE

Before 1935 all the reported work on ion exchange referred to the use of natural or synthetic inorganic exchange materials with particular reference to the softening of water.

However, after 1935, when Adams and Holmes[2] first observed that certain synthetic organic resins exhibited ion exchange properties, tremendous interest was established in these resins which resulted in the publication of a vast number of articles on the use of these resins as ion exchange materials.

As before, interest was initially centered on the use of these materials for water softening[6,9,29,48,52,89,100,78,85], but later much work was done on other applications such as pharmaceutical preparations[1,3,15,17,27,50,101,115,116] metal recovery[4,23,38,45,53,103,102], sugar refining,[16,72], food processing,[22,24,25,30,36,68,71,72,83,116], catalysis,[54,316] and various analytical applications.[7,31,91,34,19,28,35,49,51,93, 112,80,95,98,96]

The syntheses of these organic anion exchange resins are described and explained largely in patents[32,74,26,87,88], and reviews on ion exchange.[94,81,62,20].

Of particular interest are the resins in use on the Rand, i.e. the strong base quarternary ammonium compounds. A typical example is the Amberlite IRA.400 resin[74,94] which is synthesised in the following way:-

An insoluble polystyrene copolymer is prepared according to the well known principals of emulsion or suspension copolymerization in which vinyl benzene and divinyl benzene are mixed and emulsified in an aqueous salt solution containing a catalyst such as Benzoyl peroxide and heated to approximately 90°C. Insoluble spheroids of the copolymer are formed. The proportion of divinyl benzene, which acts as a crosslinking agent, determines the

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porosity, density and mechanical strength of the product. These beads of the copolymer are then swelled in an organic solvent, such as petroleum ether, and halo-alkyl groups are introduced by adding an alkyl chloride such as methyl chloride, and a Friedel Craft's catalyst such as Anhyd. $AlCl_3$, the whole mixture being stirred at 0^oC. for approximately two hours. The resulting chlormethylated beads, after drying, are refluxed with benzene, during which time the beads swell. The mixture is cooled to 25^oC. and saturated with trimethylamine gas which forms the quaternary ammonium ion exchange group.

The amount of methyl chloride that can be introduced in the halo-alkylating step depends to a large extent on the percentage crosslinking in the original copolymer. The higher the percentage crosslinking, the more difficult it is to introduce the chlormethyl group, and thus the lower the exchange capacity.

The result of such a synthesis is hard spherical insoluble particles ranging in size from 5 to 530 mesh. These are separated to a -20+60 mesh fraction, which is the range most suitable for commercial ion exchange requirements.

Variations in the above procedure include the replacement of the methyl chloride by some other alkyl halide, the use of catalysts other than $AlCl_3$ for the introduction of this alkyl halide group, and the use of various organic solvents during the preparation, which render the final product more porous.

The question of the relation between the percentage crosslinking and the ion exchange properties has been fairly extensively studied,[39,41,57,18,63] the general conclusion being that the higher the percentage crosslinking, the lower is the rate of diffusion into the centre of the particle, the lower is the total possible exchange capacity (arising from the difficulty in introducing the ion exchange groups,) but the greater is the specificity for any one particular ion.

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The properties of Amberlite IRA.400 are described by Kunin and McGarvey[61] and also in a technical bulletin issued by the manufacturers.[94] The resin is said to be as strongly basic as sodium hydroxide, and for this reason exhibits a remarkable affinity for anionic complexes and weakly acidic anions. It is effective over a pH range of 1 - 10.

It is stated to be stable in the presence of strong mineral acids and bases and insoluble in inorganic and organic solvents. The chloride salt form of Amberlite IRA.400 is stable at high temperatures, e.g. after boiling in water for eight hours. In the hydroxide form, however, it loses exchange capacity at elevated temperatures. It is recommended that when used to adsorb nitrates, the resin should be rinsed with 6% sodium chloride to restore full exchange capacity, but no reasons are given for this procedure.

Physical properties such as density, effective size, swelling, head loss characteristics and backwashing data are also provided in the above references.

The affinity of this resin for various ions has been studied by Kunin and McGarvey[61] who obtained the following series of adsorbtion affinities.

Citrate > sulphate > oxalate > iodide > nitrate > chromate > bromide > thiocyanate > chloride > formate > hydroxyl > acetate.

The properties of the Dowex I and Dowex II resins have been studied by Wheaton and Bauman[113] and F.K. Lindsay and J.S. D'Amico[67]. Properties very similar to those of the Amberlite IRA.400 are described together with the effect of crosslinking on the exchange capacity and the swelling of the resin.

Although the chemical and ion exchange properties are discussed in much detail, little information is available

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regarding the attrition resistant properties of the various resins. These are generally stated to be excellent but no figures are given to support this assertion. Several investigators have found that the replacement costs of the resins, both cationic and anionic, are higher than can be anticipated from the information of the manufacturers. Newkirk and Handelman[84] found that when using anion exchange resins for the production of dextrose by hydrolysis of starch, the capacity losses after 70, 103, 152, 209 cycles were 35.7%, 34.4%, 45.8% and 56.56% respectively. Various regenerative procedures were tried but without great success. It must be noted that the drop in capacity cited above is most likely due to poisoning of the resin rather than disintegration.

H.B. Gustafson[47] states that the replacement costs when using anion exchange resins for water treatment make up a considerable proportion of the total chemical costs. The following capacity losses of various resins (make not specified) are given.

Resins	% Capacity	Vol. tap water treated/cu. ft. resin
A, B, C	50	1,000,000
D	50	400,000
E	50	150,000

A few investigators have studied the operating costs of ion exchange installations with particular reference to water treatment. Kunin and Myers[62] describe various attrition tests and methods of determining the solubility losses of the resin

Theoretical Aspects of Ion Exchange.

The theoretical aspect of the nature of anion exchange has been extensively studied.

It has been shown by Kunin and Myers[64], Griessbach[46] and Wiklander[118] that the adsorbtion of anions by the organic anion exchange resins follow similar laws to those applicable for cation exchange resins. Most of the theoretical considerations

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have been developed for the cation exchange resins but apply in the case of the strong base anion exchange resins.

Many mathematical equations to represent the exchange equilibrium have been proposed. As yet none of these has been found to apply under all conditions encountered in ion exchange applications.

Early attempts to correlate ion exchange data with Freundlich's adsorbtion isotherm led to the relation:

$$\frac{x}{m} = k \left(\frac{c}{(a - c)}\right)^{1/p}$$ - Wiegner and Jenny.[114]

Where a = initial concentration of cations
x = quantity adsorbed
m = mass of the exchanger
c = final concentration of cations
k,p are constants.

By formal analogy with the Langmuir adsorbtion isotherm, Boyd, Schubert and Adamson[19] have proposed the equation:

$$\left(\frac{x}{m}\right)_{A^+} = \frac{kb_1\left[(Ca)^{V+}\right]^{V'+}}{1 + b_1\left[(Ca)^{V+}\right]^{V'} + b_2(Cb)^{V+}} \cdot V^+$$

Where $\left(\frac{x}{m}\right)_{A^+}$ = Amount of A^+ ion adsorbed per unit wt. of exchanger.

(Ca) & (Cb) = Activities of ions in equilibrium solution

k = Constant identified as the total exchange capacity

V, V' - are the valence states of the ions involved.

b_1, b_2 - are the constants related to the energy of adsorbtion of the cations.

Jenny[55] has applied a statistical approach to derive an equation relating the exchange of two ions of equal valency and derived the following equation:

$$w = \frac{+ S + N \pm \sqrt{(S + N)^2 - 4SN\left(1 - \frac{vw}{vb}\right)}}{2\left(1 - \frac{vw}{vb}\right)}$$

Where w = No. of cations exchanged at equilibrium

N = No. of cations added initially

S = Saturation capacity

vw, vb = Constants for each ion

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More recently Boyd and co-workers[19] have applied a rigorous interpretation of the law of mass action to the phenomena of ion exchange.

For the exchange represented by the equation

$$A^{Vb} + \left(\frac{Va}{Vb}\right) BR = AR + \left(\frac{Va}{Vb}\right) B^{Vb}$$

He obtained the relation:

$$K = \frac{(a_B v')^{va/vb} \cdot X_{AR}}{a_A v \ (X_{BR})^{va/vb}}$$

where

K	=	Thermodynamic equilibrium constant
a_A, a_B	=	activities of ions A & B
va, vb	=	valence of ions A & B
X_{AR}, X_{BR}	=	mol fractions of A & B in the exchange

This latter equation probably provides the nearest approach to the correct mathematical interpretation of ion exchange data, but tremendous difficulty is encountered in rigorously applying such relations, particularly when the degree of swelling of the exchanger is taken into account.

Gregor[43] approaching the problem from a thermodynamic point of view arrives at the equation:

$$RT \ Ln \left(\frac{a_A}{a_B}\right)_i \left(\frac{a_A}{a_B}\right)_o = p(\overline{V}_B - \overline{V}_A)$$

where p = Swelling pressure
a = Thermodynamic activity
i = Resin phase
o = Solution phase
$\overline{V}$ = Specific ionic volume

Ionic Exchange Affinity

The differences in the ion exchange behaviour of various anions and cations has been attributed by Jenny[55] and Nachod and Wood[82] to the relative charges and ionic radii of the two ions entering into the exchange. Boyd[19] and Wiklander[118] suggest that the exchange affinities reflect merely the activity of the ions. Boyd has found that the exchange affinity is inversely proportional to α the Debye-Hückel parameter.

The affinity of the resin for OH^- or H^+ depends on the

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basic or acid strength of the ion exchange resin.[64]

Anion Exchange Kinetics.

Kunin and Myers[62,65] have shown that the rate of reaction is controlled by the diffusion of the ions into the resin particles and therefore dependant on such factors as particle size, concentration, temperature and degree of saturation of the exchange capacity. For example, in the case of particles of the same diameter it has been found that:

$$\frac{Yt}{Y_\infty} = K\sqrt{t}$$

where Yt and Y_∞ are the number of milliequivalents adsorbed at time t and equilibrium respectively. K is a constant that varies linearly with the reciprocal of the particle diameter. This is in agreement with Barrer's Parabolic diffusion Law[10]. Similar results have been obtained by Boyd and his co-workers[18,19]. The relation between the rate of exchange and concentration depends on the extent of exchange.[65] The initial rate relationship can be expressed as:

$$\left(\frac{dy}{dt}\right)_0 = KC$$

The more general equation depends on the ion species. For example in the case of Amberlite IR4B, the rates of exchange can be expressed as follows[65]:

$\left(\frac{dy}{dt}\right) = KC(Y_\infty - Yt)$ .. for HCl & CH_3COOH

$\left(\frac{dy}{dt}\right) = KC^{\frac{1}{2}}(Y_\infty - Yt)$ - for H_2SO_4

$Ln\left(\frac{dy}{dt}\right) = K\ Ln\ C(Y_\infty - Yt)$ - for H_3PO_4

Kinetics of Fixed Bed Ion Exchange:

Attempts have been made to predict the performance of ion exchange columns operating under non equilibrium conditions. Thomas HC[105, 106] has derived a fully mathematical treatment, but in order to enable solution of the complex differential equation obtained many simplifying assumptions have had to be

15/ made.....

made. His derivation thus only applies to certain isolated cases, which do not include the performance of anion exchange resin columns as encountered on the Rand. Considerable attention has been devoted by Gluekauf and Duncan,[40] Boyd,[18] Mayer and Tompkins,[7] and Sillen, Ekedahl and Hogfeldt[99] to the theoretical interpretation of fixed bed ion exchange data, but in spite of these contributions the investigation has not yet reached the stage where anything but the simplest ion exchange processes can be dealt with on a theoretical basis.

For this reason any immediate possibility of a mathematical interpretation of the behaviour of ion exchange resins operating on the Rand Leach liquors (where a complex anion is being adsorbed from a large number of competing anions) can be abandoned.

A more practical approach has recently been provided by Michaels[76], where the problem has been studied on a semi-empirical basis. His interpretation of the exchange mechanism depends on the assumption of an exchange zone being established in the resin column, and from empirical data concerning the exchange zone height and its rate of movement down the column, column performance can be predicted. Although this method has only been tested for the simple Hydrogen sodium exchange on cation resins, this treatment offers the most promising basis for the design and interpretation of column performance on the Rand ion exchange applications.

For a comprehensive treatment of Ion Exchange in all its applications the reader is referred to two books, by Kunin and Myers,[64] and Nachod[81] and a review by Boyd.[20]

16/ THE....

THE PROPERTIES OF ION EXCHANGE RESINS OF PARTICULAR INTEREST TO URANIUM EXTRACTION.

The literature contains descriptions of many standard tests whereby the value of ion exchange resins for any particular application can be assessed[12,44,56,61,62,67,107,108]. In the particular application of the extraction of uranium, these standard tests have had to be modified and enlarged to include those properties of the resins which are of specific interest in this application. It is considered necessary to define, rather carefully, certain terms which have previously been rather loosely applied to other exchange applications but which have special significance in the extraction of uranium from Rand leach liquors. It has also been necessary to define new terms for particular properties of these resins which are of interest only in the extraction of uranium.

The following are definitions and brief descriptions of the various terms used in this investigation.

(1) Total Exchange Capacity.

This term is defined as the total number of exchange groups, measured in milliequivalents per gram of dry resin, present on the resin.

The commonly accepted method of measuring the total exchange capacity of these anion exchange resins is to convert them to the hydroxide form, which is then eluted with a known excess of standard acid, the excess acid in the effluent after complete elution being determined by titration. This method has not been found to be suitable for the measurement of the total exchange capacity of resins used on the Rand, since on these resins poisons are present which either react with, or are not displaced by, the OH^- ion, and consequently prevent the total number of ion exchange groups being determined. It has been found

17/ preferable...

preferable to determine the total exchange capacity by means of an analysis of the resin for total nitrogen. It has been shown[55] that in the case of the strong base anion exchange resins used on the Rand, the total nitrogen can be taken to represent the total number of exchange groups. In other words, all the amino groups on the resin are capable of undergoing exchange reactions. Even this method is not without complications, since one particular poison occurring on the resins was found to contain nitrogen, but this, as will be shown later, can be allowed for by calculation of the nitrogen associated with this poison.

(2) Chloride Capacity.

This term is defined as the number of chloride equivalents adsorbed by one gram of resin in apparent equilibrium with a 1.0N hydrochloric solution.

In the case of a fresh strong based anion exchange resin, the chloride capacity is virtually equal to the total exchange capacity. However it has been found that certain poisons are not readily displaced by the chloride ion and thus in the case of resins containing these poisons, the chloride capacity is less than the total exchange capacity.

It must be noted that, theoretically, according to the laws relating the exchange of ions on exchange resins, any one ion is capable of eluting or removing any other ion under conditions encountered in column elution; e.g. in passing a 1.0N solution of hydrochloric acid through a column of resin containing, say, a poison, the chloride adsorbed is continually being replaced by more chloride ions, whereas the poison exchanged is being continually removed from the resin column. Thus, although the exchange coefficient be exceedingly small, the passage of a large excess of the hydrochloric solution will theoretically bring about the complete elution of the poison. However, it has been observed that in the case of the poisons encountered in

this investigation, the exchange taking place between these poisons and the chloride ion is so minute, even under these conditions, that for practical purposes apparent equilibrium is attained before an appreciable quantity of poison has been remove

(3) Uranium Capacity.

This term is defined as the weight of uranium (as U_3O_8) adsorbed by 1 gram of dry resin when in apparent equilibrium with a solution containing uranyl and sulphate ions under certain specified conditions.

The amount of uranium adsorbed by a resin depends not only on the capacity of the resin but also on the nature of the solution from which adsorbtion takes place. It is necessary, therefore, to standardise certain conditions such as the pH of the solution, the temperature, and the concentration of uranium and sulphate in order to obtain true comparative values of the uranium capacity. These conditions are given in the detailed experimental method on page 127.

In most instances the uranium capacity of a resin is equivalent to the chloride capacity. In certain important cases, however, the uranium capacity of a poisoned resin is less than the corresponding equivalent chloride capacity. An explanation for this phenomenon will be discussed later.

The uranium capacity test was designed to represent the usefulness of the anion exchange resin for this particular application of isolating uranium from the Rand leach liquors.

It has been found convenient to express the uranium and chloride capacities of poisoned resins in terms of a percentage of the corresponding fresh resin's capacity, in which case they can be referred to as the "percentage uranium capacity" or "percentage chloride capacity".

For the purposes of this investigation, it is necessary

19/ to...

to distinguish between the various ways in which an anion exchange resin column may decrease in its ability to remove uranium from the Rand leach liquors as follows:

(1) Degredation of the Functional Groups. This term implies in the case of anion exchange resin the loss of some of its active amino exchange groups; i.e. the resin exhibits a decrease in the total exchange capacity.

(2) Chemical Poisoning. A chemical poison is defined as a substance, which, by virtue of its strong chemical affinity for the anion exchange groups of the resin, is incompletely eluted from the resin after complete uranium elution by the standard nitrate eluting solution, and thus causes a decrease in the uranium capacity of the resin in subsequent adsorbtion cycles.

This definition excludes substances such as the ferric anionic complex, which are adsorbed together with the uranium from a pregnant solution, but are completely eluted by the nitrate eluting solution.

The presence of a chemical poisoning is indicated by a decrease in both the chloride and uranium capacity of the resin. Strictly speaking, the extent of chemical poisoning on the resin should, most accurately, be measured by an analysis of the resin, after elution of uranium, for nitrate. The presence of a chemical poisoning would decrease the amount of nitrate capable of being adsorbed by the unpoisoned resin during elution, and this decrease would thus represent the amount of chemical poison on the resin. However, in practice it is far more convenient to elute the resin with 1.0N HCl until free of uranium and then determine the chloride remaining on the resin, i.e. the chloride capacity. In view of the very similar ion exchange properties of the chloride and nitrate anions, this method can be expected to give a good measurement of the extent of poisoning.

20/ (3) PHYSICAL...

(3) Physical Poisoning. A physical poison is defined as an insoluble substance which is precipitated or deposited on or inside the resin particles, resulting in a mechanical blocking of the ion exchange groups.

It can be appreciated that such a poison would affect the large uranyl sulphate complex anion to a greater extent than the small mobile chloride ion. In such cases the percentage uranium capacity would be lower than the percentage chloride capacity and the presence of a physical poison thus indicated.

In this investigation such a discrepancy between the uranium and chloride capacity has been found to correspond with the presence of insoluble material on the resin, and has in fact been used to indicate the presence of a physical poison.

(4) Resin Disintegration Losses. By this term is meant the resin losses due to the disintegration of the resin into very fine particles and their consequent removal from the column during the backwashing operation. It would also include resin losses due to actual solubility of the resin in the various solutions used in the ion exchange process.

S E C T I O N A .

A STUDY OF THE POISONING OCCURRING ON THE WESTERN REEFS PILOT PLANT AND WEST RAND CONSOLIDATED ANION EXCHANGE RESINS, AMBERLITE IRA.400

A STUDY OF THE POISONING OCCURRING ON THE WESTERN REEFS PILOT PLANT ANION EXCHANGE RESINS, AMBERLITE IRA.400.

PART I.

THE OCCURRENCE OF THE POISONING AND METHODS OF REGENERATION.

(1) OCCURRENCE OF THE POISONING:

In May, 1951, the Western Reefs Pilot Plant experienced a sudden deterioration in the Uranium adsorbtion properties of their anion exchange resins.[135] This deterioration occurred after approximately 10 cycles operation. Up to this time, the resin, besides showing an initial slight drop in capacity, (which appears to be a usual occurrence with fresh resins) had worked uniformly, adsorbing uranium from approximately 3,000 gallons of pregnant solution before breakthrough occurred. The flow rate in use at this time was 25 lbs. of solution per minute.

At the 11th cycle the adsorbtion proceeded normally while the first two columns, A and B, were in series and also during the period when B and C were being loaded. On changing to adsorbtion on columns C and A, (which had in the meanwhile been eluted) breakthrough occurred at a lower throughput of pregnant solution.

Thereafter, the capacity of the resins deteriorated still further when a breakthrough value of 0.065 gms U_3O_8/l. (compared with the usual 0.005 gms U_3O_8/l.) occurred after only 1,020 gallons of pregnant solution had passed through each column.

In an attempt to regenerate the poisoned resin, the users subjected them to a 2N HCl wash, which resulted in only a very slight improvement. It was observed during this treatment that after two hours in contact with the resin, nitrous fumes were evolved from the HCl solution.

Samples of these poisoned resins were then sent to the

22/ Government.....

Government Metallurgical Laboratory for investigation.

(2) EXPERIMENTAL INVESTIGATION ON THE WESTERN REEFS POISONED RESIN.

The poisoned resins received were subjected to analysis in order to determine the impurities present. In addition the capacities of the resins were measured by means of a uranium capacity test using a pure synthetic Uranium sulphate solution. It was necessary at this early stage to develop analytical methods applicable to ion exchange resins. It was also considered that the Uranium capacity test using a pure solution was to be preferred to a similar test using a pregnant solution, for the provision of information regarding the capacity of the resin. In the case of the latter solution, it was felt that the capacity would be affected by too many variables, the significance of which was not fully appreciated.

The results of these analyses are given in Table No. 1.

TABLE NO. 1.

ANALYSIS OF POISONED AMBERLITE IRA.400 RESIN RECEIVED FROM WESTERN REEFS.

	Poisoned Resin Before 2N HCl wash	Fresh Resin
1. Uranium capacity	0.114 gms. U_3O_8/gram i.e. 46%	0.349 gms U_3O_8/gram
2. Sulphur as S	3.47%	0.18%
3. Silica as SiO_2	3.21%	nil
4. Cobalt at Co	0.75%	nil
5. Fe_2O_3 and Al_2O_3	trace	trace
6. Uranium as U_3O_8	"	nil
7. Total Nitrogen	3.69 millieguiv/gram	3.83 millieguiv/gram

These analyses refer to a sample of resin in the nitrate form dried on receipt at 110°C. for 24 hours.

23/ It.....

It was noted that the water in which the resins were received contained insoluble siliceous material, colloidal sulphur and traces of cobalt.

The poisoned resin possessed a slightly darker colour than the fresh resin.

(3) REGENERATION OF THE RESIN.

The immediate requirement was for some method whereby the resin could be restored to its normal capacity so that the ion exchange columns at the Western Reefs Pilot Plant could resume operation as soon as possible. For this reason it was considered advisable to carry out regeneration tests before a fundamental study into the nature of the poison was made.

The poisoned resins were subjected to a number of chemical treatments which are summarised in Table No. 2. The Uranium capacity of the resin was measured after each treatment to obtain an idea of the effectiveness of that particular regeneration.

Initially the accepted methods of regeneration suggested by Mr. Olsen (Dow Chemical Company) were attempted. These consisted of a 6N Hydrochloric acid wash and a wash with water saturated with SO_2. Neither of these solutions produced any marked regeneration of the resin. The HCl wash gave an effluent coloured bright yellow. This colour of the solution, which contained no metallic ions, disappeared on fuming with sulphuric-perchloric acid mixture, which suggested that it was due to organic matter. This phenomenon is fairly common with cation exchange resins where it is known as "Colour throw".

As a guide to further regeneration tests, various ways in which the capacity of the resins might be reduced were considered.

24/ The.....

(i) The mechanical disintegration of the resin. This would be clearly visible and had obviously not taken place.

(ii) The mechanical blocking of the resin. This would be caused by the deposition of insoluble material on, or inside, the resin, and would prevent diffusion of the uranyl sulphate complex to the innermost ion exchange centres. Possible insoluble compounds which might produce this effect are:

(a) Insoluble silica, precipitated from the high concentrations of silicates in the pregnant solution.

(b) Insoluble decomposition products of the glue added to improve filtration of the acid leach pulp. It has on many occasions been observed that certain pregnant solutions, on standing, deposit insoluble organic material, presumably a decomposition product of the glue.

(c) Insoluble calcium sulphate. A recycled eluting solution has been found to deposit calcium sulphate on standing. This is due to the build-up of Ca^{++} and SO_4'' in the eluting solution.

(iii) The presence of an anion on the resin more strongly adsorbed than the uranyl sulphate complex, which is consequently not fully eluted by the nitrate eluting solution.

(iv) Inactivation of the amino exchange groups, either by their destruction, or by the formation of a non-ionic complex. The analysis of the resin showed no marked decrease in total nitrogen so that the former possibility can be excluded, but the presence of cobalt on the resin suggested the possibility of the formation of a non-ionic cobaltamine complex.

With the above possibilities in mind the following regenerations were attempted. The capacities of the poisoned resins after these treatments are shown in Table No. 2.

25/ TABLE NO. 2.

(i) Repeated washes of the resin in water near the boiling temperature. This treatment would remove any slightly soluble material such as calcium sulphate and, possibly, the glue disintegration products. The water effluents, however, contained no calcium sulphate nor organic matter and only a slight increase in capacity of the resin was observed. More severe conditions, such as boiling the resin in water, were not attempted since the stability of the resins at high temperatures was suspect.[61,94].

(ii) The poisoned resin was allowed to stand in cold 48% hydrofluoric acid for 16 hours. This treatment was designed to remove the silica present. The capacity of the resins increased to 60% and the HF solution, when neutralized, gave a voluminous precipitate of silica. Thus although this treatment was effective in removing the silica, the major source of poisoning had not been eliminated.

(iii) The poisoned resin was treated with 30% NaOH in the cold for two hours, washed with water, followed by nitric acid (30% v/v) to convert it to the nitrate form.

It was hoped that this treatment would have a two-fold effect, namely to provide a more practical method of silica removal, and secondly to break up any metal inorganic complexes such as cobalt thiocyanate and cobaltocyanide.

Although the capacity of the resins was increased to only 60%, the following observations suggested that regenerations of this nature should be investigated further.

(a) The NaOH effluent was found to contain a considerable amount of silica and sulphur present as a sulphide.

(b) On commencing the wash with nitric acid, bubbles of H_2S were liberated from the resin, and as the nitric acid solution reached the bottom of the column where alkaline conditions still prevailed, a black precipitate of cobalt

26/ sulphide.....

sulphide was formed. This precipitate redissolved on the passage of a further quantity of nitric acid.

Thus, part at any rate of all three of the impurities present on the resin were removed by this treatment, and it was considered possible that more severe conditions might bring about better regenerations.

The use of concentrations of the NaOH above 30% was not considered practicable since difficulty would be experienced in handling these extremely viscous and corrosive solutions on a plant scale. Heating the resin with 30% NaOH was to be avoided since preliminary tests showed that a considerable quantity of NH_3 was evolved, indicating the destruction of the amino groups on the resin.

The following further regenerations were therefore attempted :

(iv) The poisoned resin was allowed to stand in 30% NaOH at room temperature for 20 hours, followed by cold water washing followed by a 30% HNO_3 wash.

(v) The poisoned resin was allowed to stand in 30% NaOH at room temperature for 20 hours followed by a hot water wash (200 ml/gm. resin) followed by a 30% HNO_3 wash.

The capacities of the poisoned resins after these treatments increased to 78% and 90% respectively, the latter figure was considered to represent a satisfactory regeneration.

Further regenerations with lower concentrations of NaOH, or replacing the NaOH with NH_4OH, did not provide satisfactory regenerations. It appeared that the minimum requirements for efficient regeneration were as follows :

The resin should be agitated with cold 30% NaOH for not less than 20 hours. After washing with hot water (above 70°C.) for two hours, the resin should be converted to the nitrate form

27/ with.....

with 30% HNO_3. By this method regenerations of above 90% could be obtained.

The experimental results from the above series of regeneration tests are given in Table No. 2.

(4) LIFE TESTS ON THE REGENERATED RESIN.

Before the regeneration procedure could be recommended for use on the poisoned ion exchange resins at the Western Reefs Pilot Plant, it was considered advisable to carry out further tests on this regenerated resin. The possibility existed that:

(a) This somewhat severe regeneration procedure had in some way attacked the resin, which would result in its rapid deterioration when put into use.

(b) Only a superficial regeneration had been obtained which would disappear after only a few cycles of operation.

To ascertain whether either of these possibilities had occurred, it was decided to subject the resins to a number of cycles in the life tester under conditions resembling those practised at the Pilot Plant.

Accordingly, a number of poisoned and regenerated resins were subjected to loading and elution cycles similar to those used at Western Reefs as follows :

4 1" diameter columns were set up on the life tester containing approximately equal volumes of the following resins:

(a) Fresh Amberlite IRA.400 from Western Reefs.

(b) Poisoned Amberlite IRA.400 from Western Reefs.

(c) Poisoned Amberlite IRA.400 treated with 6N HCl.

(d) Poisoned Amberlite IRA.400 regenerated by the 30% NaOH treatment described above.

Each column contained approximately 40 gms. resin.

The columns were subjected to a Uranium capacity test using a pure Uranium sulphate solution similar to that described in the analytical methods of page 127.

28/ After.....

FIG. No. 1.

INITIAL LOADING CURVES. FRESH POISONED & REGENERATED. WESTERN REEF'S RESINS.

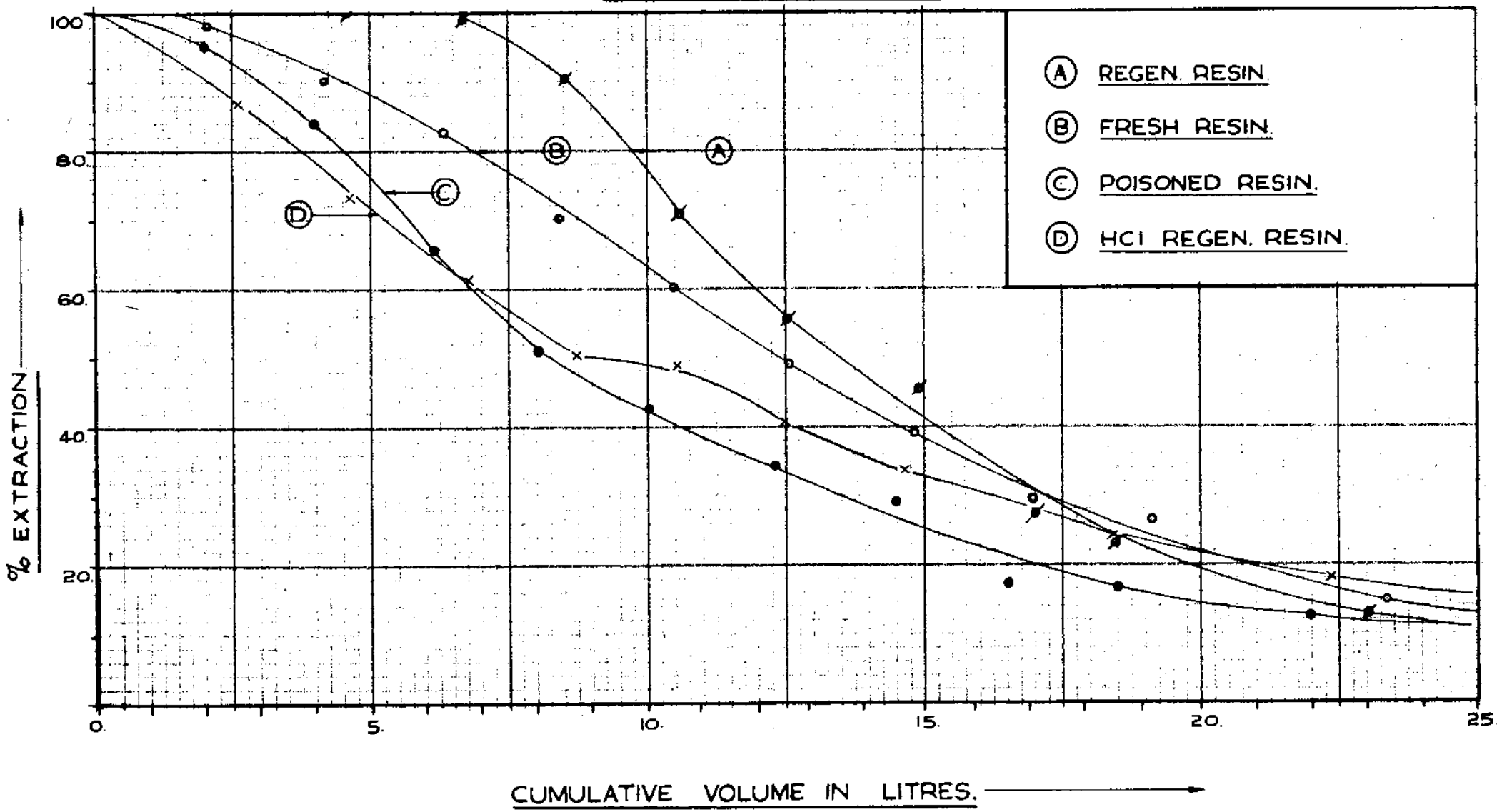
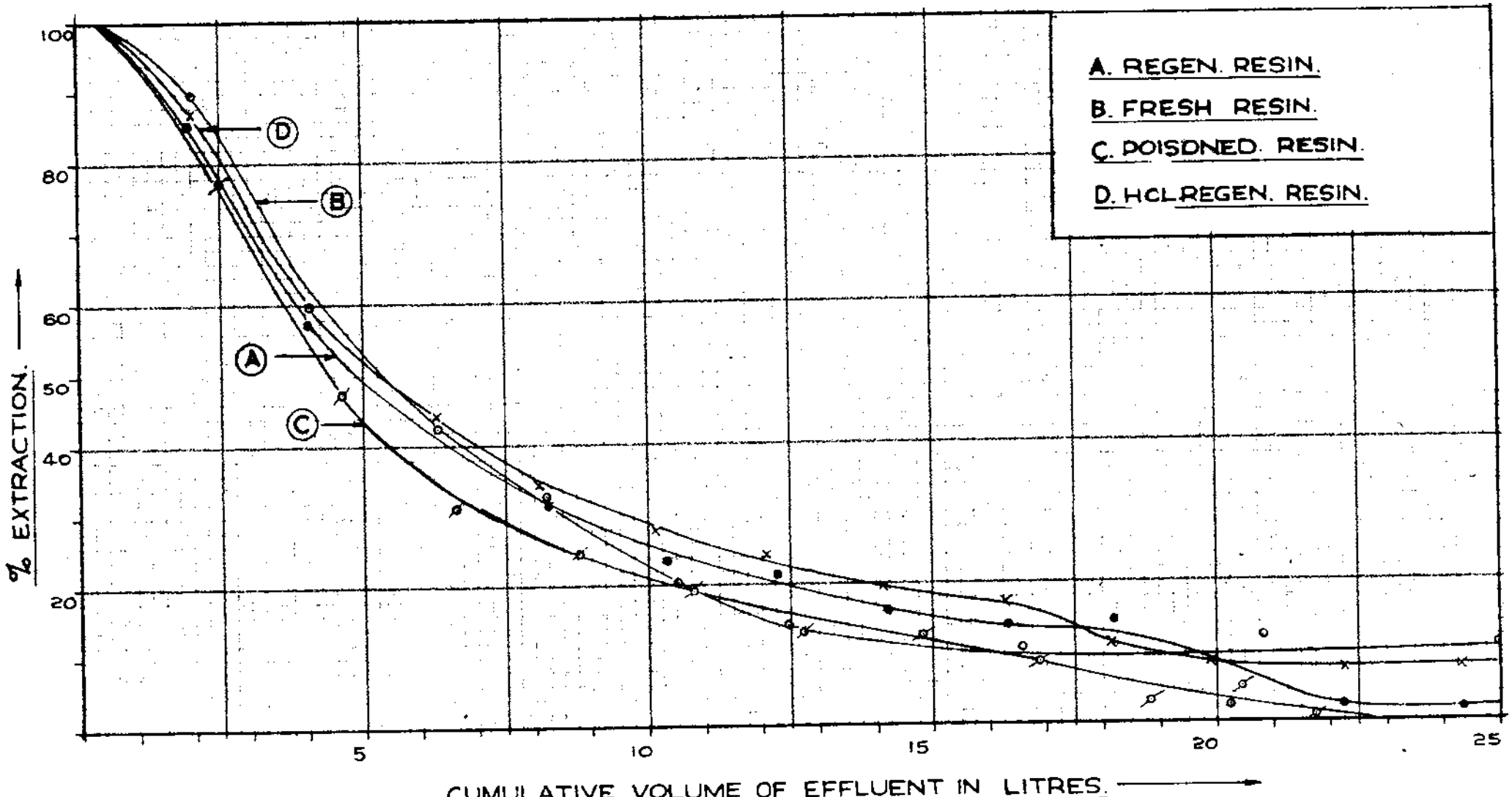


FIG. No 2

LOADING CURVES AFTER 11 CYCLES. WESTERN REEF'S POISONED, REGENERATED AND FRESH RESIN.



After elution following the Uranium capacity test, the loading curves on a Western Reefs pregnant solution were determined. This pregnant solution was claimed to represent a typical sample of the solution used on the Pilot Plant columns.

The resins were then eluted and subjected to 11 adsorbtion and elution cycles consisting of the following operations:

Adsorbtion 33 ml/min flow rate	- 8 hrs.
Down-wash " " " "	- 6 mins.
Elution with the standard nitrate eluting solution 8 ml/min flow rate	- 6 hrs.
Down-wash 33 ml/min flow rate	- 12 mins.

In addition the columns were back-washed manually every day to remove accumulated slime.

After 11 cycles the Uranium capacity and loading tests were repeated.

The results from these tests are given in Table No. 3, and Figures Nos. 1 and 2.

TABLE NO. 3.

CAPACITIES OF POISONED AND REGENERATED RESINS UNDER LIFE TEST

	COLUMN A		COLUMN B		COLUMN C		COLUMN D	
	Cap	% Cap	Cap	% Cap	Cap	% Cap	Cap	% Cap
Uranium Capacity 0 cycles	0.258	100	0.123	32	0.118	50	0.206	87
Uranium Capacity 11 cycles	0.193	82	0.155	66	0.165	70	0.197	84
Preg. Soln. Cap. 11 cycles	0.059	-	0.043	-	0.045	-	0.056	-
Wt. of resin	42.8 grams		45.7 grams		47.92 grams		36.5 gms	

Capacity in terms of gms. U_3O_8/gm. HNO_3 dried at 110°C.

Weight in terms of gms. HNO_3 dried at 110°C.

29/ Column A.....

Column A - Fresh Amberlite IRA.400

Column B - Poisoned Amberlite IRA.400

Column C - Poisoned Amberlite IRA.400 Regenerated 6 N HCl

Column D - Poisoned Amberlite IRA.400 Regenerated 30% NaOH

The initial Uranium capacities confirmed the results obtained in the small scale tests that 30% NaOH is an effective regenerant and that 6N HCl has little regenerative effect for this type of poisoning.

The initial loading curves show that in the case of the NaOH regenerated resin even better adsorbtion characteristics than the fresh resin are evident. This is indicative of a faster adsorbtion rate which suggests that the resin has been activated, possibly as a result of the swelling produced by the regeneration.

The loading curves after 11 cycles show that these improved adsorbtion characteristics of the regenerated resin have disappeared, the curves obtained in each of the four columns being very similar.

The capacities after 11 cycles show that :

(a) The capacity of the fresh resin has dropped by 18%. This drop in capacity during the first few cycles operation had also been observed in tests on Blyvooruitzicht pregnant solutions. (See page 107)

(b) The NaOH regenerated resin has maintained its capacity at approximately 85% of the fresh resin's capacity.

(c) The capacities of the poisoned resins in Columns B and C have increased to 66% and 70% respectively, i.e. a certain amount of self regeneration had taken place.

As a result of these tests it was apparent that the 30% NaOH regeneration had not adversely affected the resin and that

30/ its.....

its use on the Pilot Plant could be safely recommended.

This regeneration was carried out at the Western Reefs Pilot Plant and the poisoned columns were successfully restored to their normal working capacity.[137]

(5) FURTHER REGENERATION TESTS.

While attempting to artificially poison samples of fresh resin, a different regeneration technique was developed.

The evolution of H_2S on acid washing the 30% NaOH regenerated resin, suggested that a sulphide could in part be responsible for the poisoning of the resins. An attempt was made to artificially poison resins by passing solutions of sulphides through columns of fresh and regenerated resins. No success was obtained in poisoning the resins, in fact it was found that the passage of Na_2S had actually increased the capacity of the regenerated resin.

Accordingly, experiments were carried out on the poisoned resins using Na_2S and water saturated with H_2S as regenerants. The results of these experiments (given in Table No. 4) show that both Na_2S and H_2S were effective regenerants.

The Na_2S gave effective regenerations at much lower concentrations than those required when NaOH alone was used. Adequate regeneration was obtained with a solution of 5% Na_2S.

The water saturated with H_2S regeneration when followed by an NaOH wash gave capacities as high as 94% of that of the fresh resin.

These tests were carried out on samples of the original poisoned resin from Western Reefs which had been standing in distilled water for approximately two weeks. Uranium capacity tests on the resin after standing showed that a certain amount of self regeneration had occurred during this period. The capacity after forty days standing rose to 56%.

TABLE NO. 4

TABLE NO. 4.

FURTHER REGENERATIONS TESTS ON WESTERN REEFS

AND BLYVOORUITZICHT POISONED RESINS

NO.	TEST CONDITION	URANIUM CAPACITY gm. U_3O_8/ RESIN	% CAP
1.	Fresh Resin from Western Reefs	0.21	100
2.	Poisoned Resin from Western Reefs, HCl washed, stored under H_2O for 14 days	0.1	50
3.	Poisoned Resin from Western Reefs, HCl washed, stored under H_2O for 40 days	0.1	56
4.	Resin (2) treated with 5% NaOH for 48 hours, followed by hot H_2O wash	0.15	63
5.	Resin (2) treated with 10% NaOH for 48 hours, followed by hot H_2O wash	0.15	62
6.	Resin (2) treated with 20% NaOH for 48 hours, followed by hot H_2O wash	0.15	63
7.	Resin (2) treated with 30% NaOH for 24 hours, followed by hot H_2O wash	0.21	87
8.	Resin (2) treated with saturated H_2S water, followed by 10% HNO_3 wash	0.20	84
9.	Resin (2) treated with 20% Na_2S for 24 hours, washed and eluted with 10% HNO_3	0.21	87
10.	Resin (2) treated with saturated H_2S water, followed by 30% NaOH, washed and eluted.	0.23	94
11.	Resin (2) treated with cold 5% Na_2S for 24 hrs, washed, eluted with 10% HNO_3	0.19	78
12.	Resin (2) treated with hot 5% Na_2S, washed, eluted with 10% HNO_3	0.19	77
13.	Resin (2) treated with cold 10% Na_2S for 24 hours, washed and eluted with 10% HNO_3.	0.20	81
14.	Resin (2) treated with cold 3% Na_2S for 24 hours, washed, eluted with 10% HNO_3	0.18	72
15.	Blyvooruitzicht poisoned resins washed free of slime and sulphur.	0.18	74
16.	Resin (15) treated with 30% NaOH for 24 hours, washed, eluted with 10% HNO_3	0.22	88

The presence of cobalt was detected in the water under which the resins had been stored. An analysis of this resin after standing showed that it contained only 0.5% Co, compared with 0.75% when it was initially received. Analysis of the original 30% NaOH regenerated resin showed that it contained 0.56% Co, and further regenerations failed to produce any further removal of Co. The results of the above regenerations are summarised in Table No. 4. This Table includes regeneration tests on a sample of resin from the Blyvooruitzicht Pilot Plant, which was suspected of being poisoned. Capacity tests showed, however, that the poisoning was not serious, the capacity being 74%. 30% NaOH regeneration increased the capacity to 88%.

(6) SUMMARY AND DISCUSSION OF THE REGENERATION TESTS.

Having satisfied the immediate requirements of obtaining a suitable regeneration procedure it was decided that a fundamental investigation into the nature of the poisons occurring on the Western Reefs resin would be of value in devising further regeneration methods and means of eliminating the causes of the poisoning. For this reason further regeneration tests were not continued and the results obtained at this stage are summarised briefly below:

(1) The poisoned resin can be effectively regenerated with 30% NaOH or 5% Na_2S.

(2) The 30% NaOH treatment did not remove all the impurities on the resin. An analysis of the poisoned resin before and after NaOH regeneration is given below in Table No. 5.

TABLE NO. 5

TABLE NO. 5

ANALYSIS OF POISONED RESINS BEFORE AND AFTER REGENERATION WITH 30% NaOH

IMPURITIES PRESENT	BEFORE REGENERATION	AFTER REGENERATION
Cobalt as Co.	0.76%	0.56%
Silica as SiO_2	3.29%	0.50%
Sulphur as S	3.47%	2.30%

The analysis was carried out immediately after the 30% NaOH treatment.

(3) The ion exchange properties of the resin are in no way adversely affected by the 30% NaOH treatment.

(4) After a certain number of Uranium extraction cycles, the poisoned resin undergoes a small amount of self-regeneration, the capacity increasing from 32% to 66%. A similar self-regeneration occurs when the resin is stored under water for a period of 40 days, the capacity increasing to 56%.

(5) The capacity of a fresh resin operating on Western Reefs pregnant solution drops to 85% over a period of 11 cycles.

These results indicate that the poisoning is partly of a reversible nature. In other words, when the conditions favouring the poisoning of the resin (such as the presence of a strongly adsorbed ion in the pregnant solution) are eliminated, the particular compound causing the poisoning tends to be removed from the resin. However, only a portion of the impurities present appear to be readily removable in this way.

PART II.

THE INVESTIGATION INTO THE NATURE OF THE POISONS PRESENT ON THE WESTERN REEFS RESIN.

The tests described below were carried out on samples of Western Reefs anion exchange resins recieved periodically from the Pilot Plant. Some of these samples exhibited greater degrees of poisoning than others, but all of them contained the elements cobalt, sulphur and silica as impurities. A description of the samples together with the amount of impurities present and their Uranium and Chloride capacities are given in Table No. 6.

(1) METHODS USED IN THE INVESTIGATION

The standard methods of qualitative analysis for unknown compounds could not be applied directly to the compounds occurring on the anion exchange resins. The ion exchange properties of these resins introduce too many complicating factors. In addition it is virtually impossible to observe the formation of precipitates upon which such a scheme of analysis depends.

Certain non-volatile elements such as cobalt and silica had already been determined by ashing the resin, but of course this had destroyed the particular compound causing the poisoning. Also by modifications of standard methods of analysis other elements such as sulphur and nitrogen could be determined, but here again, these methods involved the destruction of the poison.

Initially there appeared to be three methods whereby the compounds on the resin could be identified:

(1) By eluting the poisons from the resins by means of some eluting agent, which if possible would not bring about their decomposition, followed by a qualitative analysis of the eluate. Even if the particular eluant brought about an alteration of the poison, analysis of the eluate would provide

TABLE NO. 6

valuable data regarding the poisoning.

(2) By a quantitative analysis of the resins themselves for the elements present in the poisons and attempting to correlate the molecular proportions of these elements with known chemical compounds.

(3) By a trial and error method in which attempts would be made to produce an artificially poisoned resin with the same properties as that from Western Reefs.

(2) THE NATURE OF THE COBALT COMPOUND OCCURRING ON THE WESTERN REEFS RESIN.

(a) Preliminary Tests:

It appeared highly improbable that the cobaltic or cobaltous cation could, as such, be adsorbed on an anion exchange resin. For example, when a typical Western Reefs pregnant solution containing 20.1 mgms of Co^{++}, was passed through an Amberlite IRA.400 column, no cobalt was adsorbed by the resin. Adsorbtion only occurred as a complexed anionic form of cobalt. The three most common cobalt complexes are the cobalti- and cobaltocyanides, the cobaltinitrites and the cobalt thiocyanate

Preliminary qualitative tests on the 30/ NaOH effluent, which had been found to remove a small fraction of the cobalt, failed to show the presence of any of these compounds, or any thiocyanate, nitrite or cyanide. Nevertheless, the possibility existed that the NaOH had brought about the decomposition of these compounds and their presence on the resin could not therefore be excluded.

In view of the facts that (a) the two impurities incompletely removed by the NaOH regeneration were cobalt and sulphur, in the mol. ratio of Co/S = 1/8.3, and that (b) traces of thiocyanate anions had been detected in Western Reefs pregnant solutions, it seemed likely that the cobalti-thiocyanate complex would offer the most promising line of

35/ investigation.

investigation. The presence of $Co(CNS)_6^{'''}$, as the possible complex, would require a mol ratio of Co/S = 1/6, but the observed ratio could be readily explained by the presence of other forms of sulphur. Experiments were therefore undertaken to determine if additions of thiocyanate to a pregnant solution containing cobalt would produce cobalt adsorbtion on the passage of such a solution through an anion exchange resin column.

(b) Additions of Complexing Agents to the Pregnant Solution.

Ammonium thiocyanate was added to 1 litre of Western Reefs pregnant solution containing 20·1 mgms. of Co. This solution was stirred with 1 gm of fresh resin and in repeat experiments passed through a column containing 2 gms. of resin. In every case the solutions and the resin were analysed for cobalt.

Under these conditions no cobalt adsorbtion was observed to have taken place. In each case the bright red colour of a ferric thiocyanate anionic complex was formed and strongly adsorbed by the resin. Other tests under slightly different experimental conditions produced the same result. These results are shown in detail in Table No. 16 Tests No. C1 - C5 which, for the sake of clarity, are included together with all other experimental details in an appendix at the end of this chapter.

It was therefore concluded, that the cobalt thiocyanate complex would not be adsorbed by the anion exchange resins in the presence of large amounts of Fe^{+++}.

The possibility existed that the cobalt would be adsorbed as a complex with some other sulphur compound which would not form a similar complex with Fe^{+++}. However, additions to a pregnant solution of thiosulphates, persulphates, sulphites, sulphides, bisulphites, hydrosulphites and the various polythionates failed to produce any cobalt adsorbtion on the resin. (See Tests C12 to C20). Attempts to produce these compounds

36/ 'in situ'.....

'in situ' by bubbling H_2S and SO_2 throughtthe pregnant solution under various conditions also failed to result in any cobalt adsorbtion on the resin. (Test C6 - C11, Table No 16)

The other common complexing agents present are the cyanide and nitrite anions. Their presence in a pregnant solution can be readily explained. The cyanide ion is derived from the previous cyanidation of the ore; and the nitrite may be introduced when the first portion of the eluate is returned to the pregnant solution. Any reducing agents, such as sulphur compounds, on the resin might form nitric oxides and nitrites with the nitric acid in the eluting solution. However, the addition of NaCN and $NaNO_3$ to the pregnant solution failed to result in any cobalt adsorbtion on the resin. (Tests C21 and C22 - Table No. 16).

Additions of other complexing agents such as ortho-, meta- and pyrophosphates, fluorides, silicates and silicofluorides also failed to result in any cobalt adsorbtion on the resin. (Tests C23 - C28, Table No. 16).

In view of the failure of these tests, this method of approach was abandoned and a means of removing the cobalt from the poisoned resins was sought.

(c) Attempts to Remove the Cobalt Adsorbed on the Poisoned Resins.

The accepted eluting reagents such as HCl, HNO_3, H_2SO_4, NaOH and $HClO_4$ both in dilute and concentrated solutions were found to be ineffective, only about 10% to 20% of the cobalt on the resin being removed. The perchlorate anion is a strong eluting agent and is capable of displacing most other anions. Its failure to do so in the case of the cobalt complex anion suggested that its removal depended on reactions other than a straightforward electrovalent exchange.

Most promising of these methods involved the destruction

37/ of.....

of the complex on the resin when the solution could be analysed for the products of the decomposition; e.g. if the cobalt were present as the cobalt thiocyanate complex it could be removed by oxidation of the thiocyanate (with, say, Br_2) to sulphate, thus breaking the complex into a cation Co^{+++} and an anion SO_4''. The presence of cobalt and sulphate in the solution would show that such a decomposition had occurred.

In order to examine this possibility the poisoned resin was boiled with 10% Br_2 in NaOH, when, although all the sulphur present on the resin was removed as a sulphate, only about 10% of the cobalt was removed. This showed conclusively that the cobalt was not present on the resin as a cobalt thiocyanate complex, nor as any other complex containing sulphur. Neither was it present as a cobaltinitrite since the latter would also be decomposed by this treatment. (Test C30).

Similarly, fuming the resin with hydrofluoric acid showed that all the silica could be removed without removing the major portion of the cobalt. This behaviour eliminated the possibility of complex cobalt silicates being the main cobalt complex on the resin. (Test C31.)

It is interesting to note that under these severe experimental conditions, the resin underwent no apparent decomposition as shown by the weights of the resin before and after these treatments.

Another technique has been found useful in removing ions from exchange resins, namely to elute the resins with an eluting agent which forms a complex with the ion. Although this technique is generally applied to the removal of cations from a cation exchange resin, it was considered that it might provide a possible means of removing the cobalt complex on the resin.

38/ The.....

The resin was treated with cold NaCN and cold NH_4CNS, the former being unsuccessful while the latter was found to remove 25% of the cobalt on the resin. (Test C32 and C33). This latter method showed promise since this was the greatest amount yet removed. On boiling the resin with 50% NH_4CNS, an interesting result was observed in that the resin gradually assumed a green colour similar to that of a resin loaded with cobalt thiocyanate complex anions, and even more important, that about 80% of the cobalt present on the resin was removed in the thiocyanate solution (Test C34). The green colour was, in fact, identified to be due to a cobalt thiocyanate complex and, on destroying this complex by boiling the resin with Br_2 in HCl, a further 19% of cobalt was removed, making an overall removal of 99%.

The qualitative analysis of the NH_4CNS extract was rendered extremely difficult by the high concentration of CNS^-, and also by the presence of a considerable amount of colloidal sulphur and organic matter. The colour of the extract was a deep orange-yellow. However, certain qualitative tests on this solution (Test C35) indicated that the cobalt was present as a cobalticyanide complex.

Confirmation of this indication was provided from an analysis of the poisoned resin for cobalt and total nitrogen. It had been noticed in the analyses of the various poisoned resin samples that an increase in the cobalt content was accompanied by an increase in the total nitrogen content of the resin. Analysis for total nitrogen was carried out by the Kjeldahl digestion method in which the resin was heated with conc. H_2SO_4 to convert the amino groups to ammonium salts, which were then estimated by carrying out an ammonia distillation. This treatment decomposed the cobalticyanide anion according to

the reaction:

$$2\ H_3\{Co(CN)_6\} + 8\ H_2SO_4 + 13\ H_2O = 2\ CoSO_4 + 6(NH_4)_2SO_4 + 11\ CO +$$

from which it can be seen that each equivalent of cyanide in the $\{Co(CN)_6\}$ complex forms one equivalent of an ammonium salt. A sample of the poisoned resin containing cobalt was analysed for total nitrogen by the Kjeldahl method. A sample of the same resin was then subjected to the NH_4CNS and Br_2 treatment described above to remove the cobalt, and, after thorough washing, again analysed for total nitrogen. As expected, the poisoned resin contained more nitrogen than the regenerated resin, the excess being present in an amount equivalent to approximately 6 equivalents of nitrogen to every one mol of cobalt present on the resin. (Test C36).

(d) Properties and Occurrence of the Cobalticyanide Anion.

The conclusion that the cobalticyanide anion was present on the poisoned resin explained many previously observed phenomena. The cobalticyanide anion[110] is remarkable for its great stability. It is far more stable than either the ferro- or ferricyanides, being unaffected by boiling with conc. HCl, Conc. HNO_3, chlorine, bromine and conc. NaOH. It forms insoluble salts with most of the divalent metals, but unlike the ferro- and ferricyanides, the ferric, and most of the other trivalent metal salts are soluble. It is formed by the action of CN^- on a cobalt salt to give, initially, insoluble $Co(CN)_2$ which redissolves in excess CN^- to form a cobaltocyanide. The latter anion is extremely unstable and is readily oxidised to form the stable cobalticyanide

$$Co^{++} + 2CN^- = Co(CN)_2$$

$$Co(CN)_2 + 4CN^- = Co(CN)_6''''$$

$$4\{Co(CN)_6\}'''' + O_2 + 2H_2O = 4\{Co(CN)_6\}''' + 4OH^-$$

The latter oxidation occurs very readily and can be

40/ brought...

brought about by merely allowing the solution to stand with free access to the atmospheric oxygen. It is reasonably certain that such a sequence of reactions would take place during the cyanidation of the ore, and that any cobalticyanide thus formed remaining in the cyanide residue prior to leaching, would appear unchanged in the uranium pregnant solution, and consequently cause poisoning of the anion exchange columns.

It is apparent from cobalt analyses carried out at the Western Reefs Pilot Plant that only a small portion of the total cobalt in the ore undergoes this series of reactions. The major portion is dissolved under the acid conditions of the uranium leach and appears in the pregnant solution as a cobalt cation, which has no effect on the anion exchange resins. This explains the failure in the earlier tests to obtain any cobalt adsorbtion, since in the particular batch of pregnant solution used no cobalticyanide was present although a considerable amount of the cobaltous cation was found.

The failure to detect CN^{1} on the poisoned resins in the preliminary tests was due to the remarkable stability of the cobalticyanide anion.

(3) THE NATURE OF THE SULPHUR COMPOUNDS OCCURRING ON THE WESTERN REEFS POISONED RESIN.

Preliminary Tests:

The presence of colloidal sulphur in the water under which the resins had been stored led to the suspicion that at least a part of the total sulphur on this resin was in this form. A thoroughly washed sample of the resin was extracted with CS_2 in a Soxhlet apparatus and found to contain 1·20% S soluble in CS_2. The total sulphur on this particular resin was 3·21%. No sulphate, sulphides, thiocyanates or thiosulphates were found to be present by simple qualitative tests. The tests on the nature of the cobalt poison on the resin showed that the sulphur was in no way complexed with the cobalt.

41/ Identification.....

Identification of the Sulphur Compound on the Resin.

A means of removing the sulphur compound on the resin was sought. The 30% NaOH used for regeneration, although removing part of the sulphur, must, in so doing, have altered the form of the sulphur compounds since both sulphides and thiosulphates were detected in the NaOH wash, whereas neither of these compounds was detectable on the original poisoned resin. Neither dilute nor conc. HCl was found to be effective in removing the sulphur.

However, 1·0N HNO_3 was found to remove at least part of the sulphur present without any visible signs of decomposition. Qualitative tests on this HNO_3 eluate indicated the presence of polythionates. (Test C38).

This indication was confirmed by elution of the resin with NaCN which undergoes the following reactions with polythionates.

$S_6O_6'' + 5CN' + H_2O = S_2O_3'' + SO_4'' + 3SCN' + 2HCN$ - (1)

$S_5O_6'' + 4CN' + H_2O = S_2O_3'' + SO_4'' + 2SCN' + 2HCN$ - (2)

$S_4O_6'' + 3CN' + H_2O = S_2O_3'' + SO_4'' + SCN' + 2HCN$ - (3)

The presence of CNS' and S_2O_3'' in the NaCN eluate was detected and taken to confirm the presence of polythionates.

It was considered of some importance to determine which of the polythionates was present, so that the extent of poisoning due to these compounds could be calculated from an analysis of the resin. This was thought possible by means of the reactions (1), (2) and (3) and reactions of the polythionates with SO_3''.

In just alkaline solutions the following reactions take place

$S_6O_6'' + 3SO_3'' = S_3O_6'' + 3S_2O_3''$ - (4)

$S_5O_6'' + 2SO_3'' = S_3O_6'' + 2S_2O_3''$ - (5)

$S_4O_6'' + SO_3'' = S_3O_6'' + S_2O_3''$ - (6)

42/ The....

The thiosulphate formed according to these reactions could be determined by titration with iodine, after removing the excess sulphite with formaldehyde.[42]

A sample of freshly poisoned resin was treated with solutions of just alkaline NaCN and Na_2SO_3 under a variety of conditions, and the thiosulphate thus formed determined. It was, however, found impossible to obtain duplication of results. Moreover rough estimates from these figures showed that in order to account for the total sulphur on the resin, the presence of a hexathionate would have to be assumed. This was surprising since the hexathionates are generally assumed to be unstable. The most stable of the polythionates is the tetrathionate, S_4O_6. (Test C38).

However, it was realised that errors might have been introduced by the use of alkaline solutions on a strong base anion exchange resin. In strong alkaline solutions the polythionates decompose as follows:[42]

$$S_6O_6'' \xrightarrow{(OH)'} S_5O_6'' + S \qquad - (7)$$

$$S_5O_6'' + 6OH' = 5S_2O_3'' + 3H_2O \qquad - (8)$$

$$4S_4O_6'' + 6OH' = 5S_2O_3'' + 2S_3O_6'' + 3H_2O \qquad - (9)$$

$$2S_3O_6'' + 6OH' = 4SO_3'' + S_2O_3'' + 3H_2O \qquad - (10)$$

During the passage of the slightly alkaline cyanide and sulphite solutions, the OH' would be adsorbed by the anion exchange resin with the result that inside the beads of the resin a high concentration of OH' ions would exist, and this would bring about the decomposition of the polythionates as above.

Assuming the above theory to be correct, elution of the poisoned resin with NaOH should bring about the complete decomposition of the polythionate according to reactions (7), (8), (9) and (10).

Such an experiment was carried out in which the poisoned resin was eluted with 10% NaOH, and the thiosulphate thus formed,

43/ determined....

determined. The results on duplicate determinations were in excellent agreement and it was found that the sulphur on the resin could be satisfactorily accounted for by the presence of a tetrathionate, S_4O_6''. The experimental details are given in Test C39

Occurrence of the Polythionates:

The presence of polythionates in the pregnant solutions could not be as readily accounted for as in the case of the cobalticyanides. These compounds are generally formed as a result of a reaction between H_2S and mild oxidizing agents such as Fe^{+++}, SO_2 or an MnO_2 suspension.

With the majority of the Rand ores H_2S is evolved on the addition of acid, and it was originally considered that the formation of polythionates was the result of the reaction of this gas with either the Fe^{+++} or the MnO_2 present during the uranium leach. Judging from the experience at the Western Reefs Pilot Plant where only specific batches of pregnant solution exhibited particularly bad loading properties and subsequently caused a sudden deterioration of the ion exchange columns, it seemed likely that certain conditions favoured the formation of polythionates, these conditions being absent from the majority of the leaching procedures.

Accordingly an investigation was undertaken to study the effect of certain variables on the formation of polythionates during the uranium leach. Factors such as the Fe^{+++} concentration, the acid concentration, the amount and the nature of the MnO_2 addition and the effect of air agitation were studied. None of these factors were found to have any marked effect on the polythionate formation. Samples of the cyanide residue from Western Reefs and West Rand Consolidated (which had also experienced poisoning) and the uncyanided ore from Luipaardsvlei (which in other tests had been observed to evolve much H_2S

44/ on.....

on the addition of acid) were used for these tests.

It was observed that in the case of the West Rand Consolidated and Western Reefs residues, traces of thiocyanate and cyanide ions, which were originally present in the cyanide residue, still remained in the pregnant solution after leaching. These ions interfered in the method of analysis for polythionate and steps were taken to remove them by thorough washing of the cyanide residue prior to leaching.

As a result of this treatment the polythionate formation was practically eliminated. This implied that the compound causing the formation of the polythionates was present in the original cyanide residue and could be removed by washing. In the case of the Luipaardsvlei ore, which had not yet been cyanided, virtually no polythionates were found in the pregnant solution. Detailed analysis of the recycled cyanide liquor showed that the only other sulphur compound present, apart from sulphate, was the thiocyanate anion.

It was at first considered possible that the thiocyanate acted merely as a catalyst for the formation of polythionates. However, the addition of known amounts of thiocyanate to a thoroughly washed cyanide residue prior to leaching, resulted in the formation of polythionates, the amounts of which were approximately proportional to the amount of CNS originally added.

It was, therefore, concluded that the formation of polythionates was the result of the destruction and oxidation of the thiocyanate ions present in the unwashed cyanide residue. The results of the tests described above are summarised in Table No. 7.

Properties of the Tetrathionate Ion.

Of all the polythionates, the tetrathionate is the most stable. Nevertheless pure solutions of the sodium salt of this anion decompose slowly in the cold with the deposition of

TABLE 7

THE FORMATION POLYTHIONATES

Ore Used	Wt. of Ore (gms)	Acid Added lbs/ton	MnO_2 Added lbs/ton	Time of Addition	Other Reagents Added	Temp.	ANALYSIS IN PREG. SOLN. Fe^{++} g/l	Fe^{+++} g/l	H_2SO_4 g/l	S_4O_6'' as g S/l	Remarks and Observations
Luipaardsvlei	500	30	0	Simultaneously with acid	nil	room	0.8	3.8	6.0	0.0012	Uncyanided ore used
"	"	"	10	"	"	"	nil	5.8	5.8	0.004	
"	"	"	"	"	5 lbs/t Fe^{++}	"	"	7.6	3.0	0.0088	
"	"	"	"	"	10 " "	"	"	14.0	2.2	0.0016	
Western Reefs	500	35	0	Simultaneously with acid	nil	room	1.4	0.4	8.4	0.08	Unwashed Cyanide Residue used
"	"	"	15	"	"	"	trace	1.6	5.0	0.12	Agitated in bottles on rolls
"	"	"	"	"	5 lbs/t Fe^{+++}	"	0.3	4.2	4.1	0.09	Odour of HCN after leaching
"	"	"	"	"	10 " "	"	0.6	6.8	3.9	0.13	Much CNS in pregnant solution
West Rand Consolidated	500	30	10	1 hour after acid addition	nil	5°C	-	-		0.048	Unwashed Cyanide Residue
"	"	"	"	"	"	10°C	-	-		0.064	Air agitated in pachucas
"	"	"	"	"	"	15°C	-	-		0.040	No odour of HCN
"	"	"	"	"	"	22°C	-	-		0.048	
"	"	"	"	"	"	30°C	-	-		0.056	
Western Reefs	500	35	0	1 hour after acid addition	nil	room	1.4	0.5	11.5	0.08	Unwashed cyanide residue
"	"	"	15	"	"	"	trace	1.8	7.9	0.10	Air agitated in pachucas
"	"	"	"	"	5 lbs/t Fe^{+++}	"	0.2	6.4	9.9	0.12	No odour of HCN
"	"	"	"	"	10 " "	"	0.2	9.6	7.8	0.076	Only traces of CNS' in preg. soln.
"	500	30	15	Simultaneously with acid	nil	room	nil	0.9	0.3	0.11	Unwashed Cyanide residue
"	"	40	"	"	"	"	"	1.6	4.0	0.076	Air agitated in pachuca
"	"	50	"	"	"	"	"	1.8	7.8	0.058	No odour of CN'
"	"	60	"	"	"	"	"	1.9	12.5	0.107	Only traces of CNS'
"	500	35	0	Simultaneously with acid	nil	room	0.9	0.6	8.7	0.005	Cyanide residue washed and dried
"	"	"	15	"	"	"	nil	1.7	5.6	0.006	Agitated in bottles on rolls
"	"	"	"	"	5 lbs/t Fe^{+++}	"	trace	4.6	4.8	0.008	No odour of HCN
"	"	"	"	"	10 " "	"	"	7.6	4.1	0.015	No CNS' present in preg. soln
"	500	35	15	Simultaneously with acid	0.4 gms. NH_4CNS	room	trace	1.6	5.0	0.13	Agitated in bottles on rolls Much CNS' and HCN in preg. soln.
"	500	35	15	Simultaneously with acid	0.2 lbs/t NH_4CNS	room	trace	1.6	5.3	0.021	Cyanide residue washed by repulping
"	"	"	"	"	0.6 " "	"	"	1.6	5.5	0.030	twice with water. Agitation in pachucas
"	"	"	"	"	1.2 " "	"	0.15	1.4	5.5	0.059	Odour of HCN in preg. soln.
"	"	"	"	"	2.4 " "	"	0.60	1.4	5.3	0.077	after leaching.
"	"	"	"	"	nil	"	trace	1.6	5.4	0.014	

colloidal sulphur. The decomposition is accelerated in alkaline solutions[42] and in the presence of certain impurities, notably, in this instance, sulphuric acid.[75] The tetrathionate is moderately stable in cold dilute nitric acid, but on heating is rapidly oxidised to sulphate. On standing in the presence of nitric acid in the cold, for some length of time, colloidal sulphur is formed.[75]

The tetrathionate reacts rapidly and quantitatively in alkaline solution with sulphites and cyanides as shown in reactions 3 and 6. A similar reaction occurs with alkaline sulphides according to the equation

$$S_4O_6'' + S'' = 2S_2O_3'' + S \qquad - (11)$$

Its reaction with strong alkalies has already been given (reactions 9 and 10).[42]

With strong reducing agents such as nascent hydrogen, a sulphide is formed.

With strong oxidizing agents in hot solution, polythionates are quantitatively oxidised to sulphates.[75]

When a resin in the nitrate form containing tetrathionates is allowed to stand in the cold, the tetrathionate decomposes, liberating colloidal sulphur, some of which remains inside the resin particles. Analyses of the various samples of poisoned resin from Western Reefs show that although they all contain tetrathionates, only those that have stood for some length of time contain colloidal sulphur. It can thus be assumed that the presence of this substance can be accounted for by the decomposition of the tetrathionate. The effect of this decomposition will be discussed in more detail later.

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(4) THE NATURE OF THE SILICEOUS COMPOUNDS ON THE WESTERN REEFS POISONED RESIN.

The adsorbtion of silicate ions present in the pregnant solutions by the strong base ion exchange resins was only to be expected. In fact these resins are employed in water-softening installations to remove this ion from high silica content waters.

However in this particular instance, the major amount of the silica determined in the analyses of the poisoned resins was present as an insoluble form adhering to the resin particles. This insoluble silica could only be removed, with difficulty, by washing of the resin or by elution with strong alkalies.

It is possible that part of the silica determined was present as a silicate anion adsorbed on the resin, but it was found to be impossible to distinguish between these silicates and the insoluble silica by analytical methods.

However, when the nature of the cobalt and sulphur compounds on the resin had been established, it was then possible to calculate the amount of the poisoning caused by these elements, from an analysis of the resin. In all cases the calculated capacity agreed well with the experimentally determined chloride capacity disregarding any effect of the silica. It can be concluded therefore that the silica on the resin does not play an important role in the poisoning of the resin and that the major portion is present in an inactive form attached to or inside the resin particles.

A typical analysis of a clarified pregnant solution shows that about 2/3 of the total silica is present as colloidal silica and will not give the colourimetric reaction of silicates with ammonium molybdate. The presence of this colloidal silica in the pregnant solution provides a ready explanation for the accumulation of the siliceous slime in the anion exchange

47/ columns....

columns, operating on an apparently clear pregnant solution.

It has been found in water treatment installations that the silicates, although initially adsorbed, by the strong base anion exchange resins, are readily displaced by other anions such as SO_4^{--} and CO_3^{--}, and for this reason it is considered that although the Rand leach liquors will unavoidably contain comparatively high concentrations of silicates, these will not give rise to any serious poisoning of the columns.

(5) GENERAL CONSIDERATIONS OF THE POISONING OF THE ION EXCHANGE RESINS AT WESTERN REEFS.

Having established the identity of the compounds present as impurities, on the Western Reefs resin, it was necessary to discover whether the removal of the three major impurities - Co, S, SiO_2, resulted in the complete regeneration of the resin.

Accordingly a sample of resin was (a) fumed with HF to remove all the silica, (b) boiled with 50% NH_4CNS to remove the major portion of the cobalt, (c) boiled with 10% Br_2 in HCl to remove the sulphur compounds and the remaining cobalt. The capacity was then determined and found to be 3.75 milliequivalents/gm dry RCL, which, when compared with the value of 3.6 milli-equivalents/gm RCL for a fresh resin, showed that complete regeneration had been obtained. (Test No. C40.)

It may be concluded, therefore, that the poisoning of the resin is due to the presence of the following impurities :

1. Cobalticyanide anions.
2. Tetrathionate anions.
3. Colloidal sulphur.
4. Insoluble silica.

The regenerative effect of the 30% NaOH can be considered to be due to the following reactions:

(a) It readily removes the silica from the resin.

48/ (b) It....

(b) It reacts with the tetrathionate ion as in equations (9) and (10), bringing about their decomposition and subsequent removal.

(c) It reacts with colloidal sulphur to form Na_2S, thus removing it from the resin.

An explanation why the concentrations of NaOH below 30% are not as effective is possibly as follows:

Although the reaction with polythionates in solution normally requires a high OH concentration, it has been shown that this decomposition occurs in weakly alkaline solutions in the presence of the anion exchange resins. However it can be appreciated that the solution of colloidal sulphur in alkalies requires high concentrations of NaOH because in this case it is the concentration of the Na^+ which is the important factor and this will not be influenced by the anion exchange resin.

The regenerative effect of the 5% Na_2S is similarly explained by the fact that :

(a) It is sufficiently alkaline to remove the silica.

(b) It reacts with the tetrathionate, bringing about its decomposition according to equation (11).

(c) It reacts with the colloidal sulphur to form a polysulphide.

None of these reactions requires a high concentration and hence a relatively low concentration of Na_2S is an efficient regenerant.

It has already been observed that the above regenerants have little of no effect on the cobalticyanide anion. In the original sample of poisoned resin from Western Reefs, the amount of cobalt present did not contribute appreciably to the poisoning of the resin. In subsequent samples, in which the cobalt content of the resin had built up sufficiently to be responsible for a large percentage of the poisoning, the 30% NaOH and the 5% Na_2S did not provide as efficient regeneration. This was the case in samples of Western Reefs resin after approximately 80 cycles operation (See Table No. 6), in which the cobalt content

49/ of.....

of the resin was 1.72%, which accounted for 24% of the total exchange capacity. Thus in this case, neither the 30% NaOH nor the 5% Na_2S regenerants could be expected to increase the capacity to a value above 76%.

A detailed calculation is given below to illustrate how the actual capacity can be calculated from a chemical analysis of the poisoned resin. For this calculation the last two samples of poisoned resin received from Western Reefs are considered. When these typical poisoned resin samples were examined the analytical methods for polythionates and cobalt estimations, and the determinations of chloride and uranium capacities had been perfected. These analyses were carried out immediately on receipt of the samples.

Resin A: Amberlite IRA.400. Ex Column A - Western Reefs. Fully eluted with nitrate eluting solution. 80 cycles operation. Washed with water before analysis.

Resin B: Amberlite IRA.400. Ex Column B - Western Reefs. Fully eluted with Nitrate eluting solution. 15 cycles operation. Washed with water before analysis.

ANALYSIS	RESIN A	RESIN B
Total Sulphur as S	7.23%	7.50%
Tetrathionic Sulphur as S	7.23%	7.32%
Colloidal Sulphur as S	nil	Trace
Silica as SiO_2	5.9%	4.0%
Cobalt as Co.	1.72%	1.17%
Total Ash	8.0%	4.8%
Actual U_3O_8 capacity gms. U_3O_8/gm. RNO_3	.118	.114
% U_3O_8 capacity. (Fresh resin .262 gms U_3O_8/gm.)	45%	55%
Actual Cl capacity millequiv./gm RNO_3	1.57	2.01
% Cl capacity (Fresh resin 3.6 millequiv./gm RNO_3)	44%	56%

50/ Assuming.....

Assuming that the polythionate is present as the tetrathionate S_4O_6'', then for every 32 gms. sulphur present on the resin 0.5 gm-equivalents of the resin's capacity are required to combine with this compound. Similarly for every 59 gms of Co present on the resin as $\{Co(CN)_6\}'''$, 3 gm-equivalents of the resins capacity are poisoned.

		RESIN A.	RESIN B.
Thus: Equivalents poisoned by S_4O_6'' present on 1 gm.	=	$\frac{7.23}{2 \times 32 \times 100}$	$\frac{7.32}{2 \times 32 \times 100}$
as milliequivalents capacity	=	$\frac{7.23}{6.4}$	$\frac{7.32}{6.4}$
	=	1.13	1.14
% poisoning due to S_4O_6''	=	$\frac{1.13 \times 100}{3.60}$	$\frac{1.14 \times 100}{3.60}$
	=	31.4%	31.7%
Similarly milliequivalents poisoned by cobalt on 1 gm.	=	$\frac{1.72 \times 30}{59}$	$\frac{1.17 \times 30}{59}$
	=	0.874	0.595
% poisoning due to cobalt	=	$\frac{87.4}{3.6}$	$\frac{59.5}{3.6}$
	=	24.3%	16.2%
Total poisoning due to cobalt and S_4O_6''	=	55.7%	48.9%
Calculated % capacity	=	44.3%	51.1%

It will be noted that these figures are in agreement with the experimentally determined capacities, the latter values being very slightly higher. This slight discrepancy is considered to be due to the small amount of the poison (particularly tetrathionate) removed by the solutions used in the capacity tests.

From these and other calculations it is apparent that silica plays no important part in the chemical poisoning of the resins.

Calculations on the results obtained for the original

51/ samples.....

samples of poisoned resin from Western Reefs do not, however, show similar agreement in respect to the calculated and experimentally determined capacities. It must be remembered that the analytical methods at that stage of the investigation had not been perfected and the figures obtained and quoted are subject to considerable error. Nevertheless the difference between the uranium capacity of 46%, the chloride capacity of 59% and the calculated capacity of 75.6% indicate differences beyond the range of experimental error. A possible explanation of these differences may be related to the presence of colloidal sulphur on the resin. Another sample of resin received at a later date (No. 1 H, Table No. 6) which had been allowed to stand in the nitrate form for approximately two weeks before analysis, was found to contain 2.11% of free sulphur and also exhibited a similar difference between chloride, uranium and calculated capacities. A deposition of sulphur arising from the decomposition of the tetrathionates will occur inside the resin particle and it appears likely that this substance will mechanically hinder or prevent the diffusion of the chloride and uranyl sulphate anions to the innermost exchange groups. It can be appreciated that this effect will be more pronounced in the case of the large, probably highly hydrated uranyl sulphate complex, than in the case of the small relatively mobile chloride ion. Thus a possible explanation for the difference in uranium, chloride and the calculated capacities is provided. In support of this theory, is the fact that the operators at the Western Reefs Pilot Plant observed a sudden deterioration of the resin after the ion exchange columns had been shut down for a period of two weeks, during which period the tetrathionate would have undergone decomposition accompanied by the precipitation of sulphur and the consequent decrease in capacity.

A study of Table No. 6 shows a slow but steady accumulation

52/ of....

of cobalticyanide by the resins. During the work carried out on the identification of the cobalticyanide, it was apparent that this ion was strongly adsorbed by the resin, and once adsorbed proved exceedingly difficult to remove. For this reason it must be considered to be the most serious of the poisons. In 80 cycles operation at the Western Reefs Pilot Plant, the ion exchange resins had accumulated 1.72% of cobalt. If this rate of adsorbtion is maintained the resin can be expected to be completely poisoned after 300-350 cycles. In actual practice the columns would be inadequate to extract the uranium from the amount of pregnant solution to be treated long before this number of cycles had been completed. It was essential, therefore, to obtain methods for either easily removing the cobalt from the resin or, alternatively, eliminating the cobalticyanide from the pregnant solution to be treated in the exchange columns.

Polythionate poisoning may be considered as a less serious matter. It has been shown that the tetrathionate is partially removed by nitric acid solutions, and that partial elution of this anion will thus occur during the normal uranium elution. This undoubtedly explains the self-regeneration effects observed with the first samples of the poisoned Western Reefs resin. In this instance the poisoning was almost entirely due to the presence of the tetrathionate anion and colloidal sulphur. On subjecting this resin to a further 11 extraction cycles, an increase in capacity from 32% to 66% was observed.

It was considered, therefore, that the presence of small amounts of polythionate in the pregnant solution would not have the same disastrous cumulative effect as the cobalticyanide. Moreover the regeneration of resins poisoned with polythionate presents no great difficulty, both Na_2S and NaOH being cheap and effective regenerants.

53/ (8) A STUDY...

(6) A STUDY OF THE POISONING OF THE ION EXCHANGE RESINS AT WEST RAND CONSOLIDATED URANIUM PLANT.

Introduction.

In January, 1953, a sample of West Rand Consolidated cyanide residue was received for experiments regarding the effect of temperature on leaching extraction. This sample was found to contain an appreciable amount of impurities such as thiocyanates, resulting from the previous cyanidation treatment. This indicated an incomplete washing of the cyanide residue and, in view of the results of the experiments on the poisoning of the resins at the Western Reefs Pilot Plant, it was considered advisable to analyse this cyanide residue for cobalticyanide anions.

This analysis showed an excessive amount of cobalticyanide to be present and indicated that the ion exchange resins at the West Rand Consolidated Plant were in all probability seriously poisoned.

Accordingly, samples of these resins were analysed according to the methods developed during the study of the Western Reefs poisoning. As anticipated these samples contained high percentages of cobalt and polythionates, and exhibited a considerable degree of poisoning.

Experimental Procedures and Results:

(a) Analysis of Solutions.

Samples were taken of the gold pregnant cyanide solution, the uranium pregnant solution and the recycled barren eluting solution. These were analysed for cobalticyanide with the following results:

Gold Pregnant cyanide solution - 3.8 mgms. Co/litre present as $\{Co(CN)_6\}'''$

Uranium Pregnant solution - 3.1 mgms. Co/litre present as $\{Co(CN)_6\}'''$

Recyled eluting solution - 10.1 mgms. Co/litre present as $\{Co(CN)_6\}'''$

54/ (b) Analysis...

(b) Analysis of Resin.

Samples of resin were received from each of the four sets of columns at the West Rand Consolidated Plant. The resin from set (1) was Ionac and from the other three sets, Amberlite IRA.400.

The resins were thoroughly washed with water, their uranium and chloride capacities determined, and analysed for impurities with the following results:

Analysis of Resins:

TABLE NO. 8

Impurities Present

	Cobalticyanide as Co	Tetrathionate as S	SiO_2	Fe^{+++}	AsO_4
Set (1)	1.59%	0.35%	7.49%	Trace	Trace
Set (2)	2.40%	3.65%	3.43%	"	"
Set (3)	0.66%	1.01%	5.23%	"	"
Set (4)	2.08%	2.30%	5.83%	"	"

TABLE NO. 9

Uranium and Chloride Capacities

	Uranium Capacity	Chloride Capacity
Set (1)	71.4%	62.5%
Set (2)	47.0%	46.5%
Set (3)	83.0%	80.0%
Set (4)	54.0%	53.5%

Capacities expressed as a Percentage of the corresponding fresh resins capacity.

The resins in sets (2) and (4) had been in use from the time Plant operation had commenced, while the resins from sets (1) and (3) had only recently been put into operation. It is estimated that sets (2) and (4) had undergone 35 extraction cycles.

55/ Discussion....

Discussion of Results:

As in the case of the Western Reefs poisoning the theoretical capacity can be calculated from the analysis of the resin.

TABLE NO 10.

Calculated Capacities of West Rand Consolidated Resins

	Calculated Poisoning due to $(Co(CN)_6)'''$	Calculated Poisoning due to S_4O_6''	TOTAL	Capacity Calc.	Capacity Found
Set (1)	25%	1.7%	27%	73%	71%
Set (2)	35%	15.8%	51%	49%	47%
Set (3)	9%	4.4%	14%	86%	83%
Set (4)	29%	12.6%	41%	59%	54%

The extent of any poisoning due to SiO_2 cannot be accurately calculated since the major portion of the silica is present as insoluble SiO_2 adhering to the resin.

It may be observed that the calculated capacities agree reasonable well with the experimentally determined capacities.

It may, therefore, be accepted that the cause of the poisoning occurring at the West Rand Consolidated Plant is exactly similar to that occurring at the Western Reefs Pilot Plant and is due to the adsorbtion of cobalticyanide and polythionate anions by the resin.

It was later learned that at the West Rand Consolidated Plant no washing step had been provided after cyanidation and prior to the acid uranium leach. The cyanide residues were merely given a barren cyanide liquor wash prior to leaching. This was undoubtedly the main contributing factor to the exceptional degree of poisoning occurring on the West Rand Consolidated ion exchange resins, since as a result of this procedure, both cobalticyanide and thiocyanate (which are both formed

56/ during....

during the cyanidation) are introduced into the acid uranium leach, the latter ion forming polythionates during the leaching procedure.

PART III

METHODS OF ELIMINATING THE COBALTICYANIDE AND POLYTHIONATE POISONING OF THE ION EXCHANGE RESINS.

An investigation was undertaken with the object of evolving a method whereby the poisoning of the ion exchange columns could be eliminated. The investigation was originally commenced on the Western Reefs Ion exchange resins, but the appreciation of the serious nature of the poisoning at the West Rand Consolidated Plant immediately focussed the attention of many other investigators on the problem of eliminating the poisonsat this plant.

There appeared to be two different methods of approaching the problem. The first was to develop cheap and efficient methods for removing the poisons (particularly the cobalticyanide anion) from the ion exchange resins. This would enable the resins to be regenerated, say every ten cycles, and restored to their normal working capacity, so that the accumulation of the poisons would never reach the stage where it would seriously interfere with uranium extraction.

The second was to provide efficient means of eliminating the poison before it came into contact with the ion exchange resins.

The latter alternative appeared to offer the most promising line of investigation, but the prospect of having to discard a large quantity of the already poisoned resin at the West Rand Consolidated Plant, stimulated research into the regeneration methods.

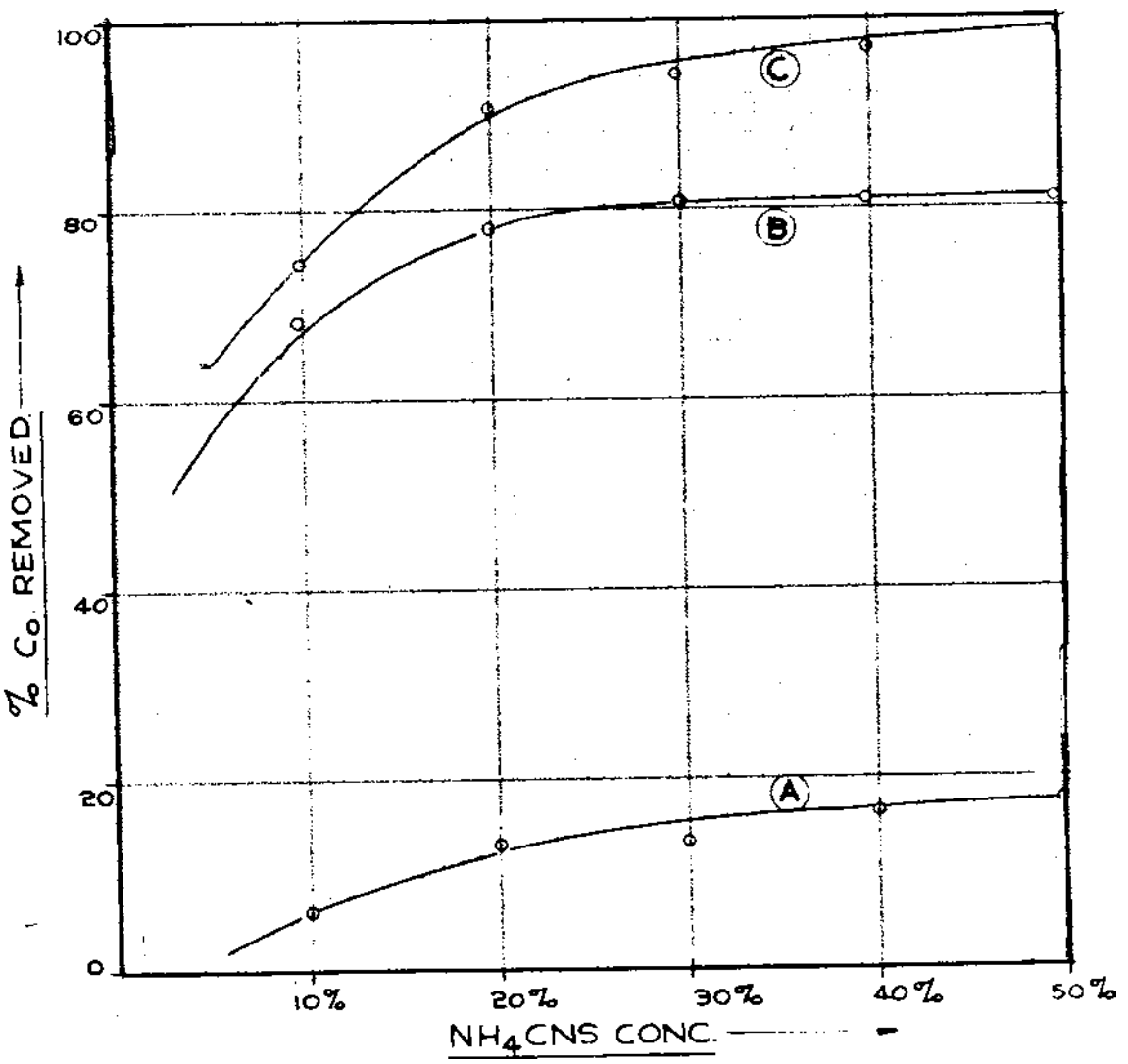
1. METHODS OF REGENERATING THE POISONED RESINS.

Although the methods of regeneration already developed, consisting of a 30% NaOH wash or a 5% Na_2S wash, were suitable

58/ for...

FIG. No. 3

TEST C41 EFFECT OF NH_4CNS CONC. ON C_o REMOVAL.



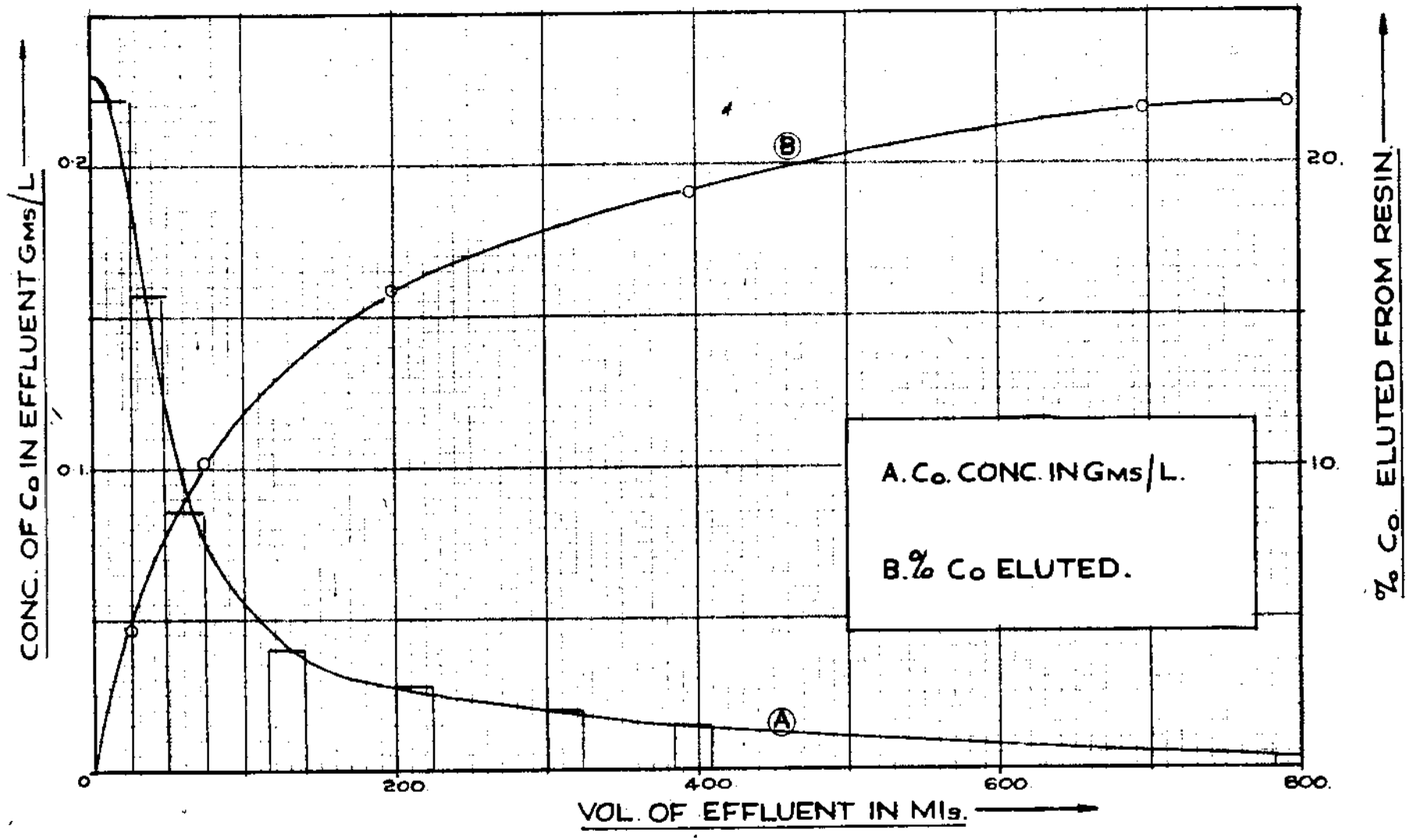
A. C_o REMOVED IN Br_2 WASH

B. C_o REMOVED IN NH_4CNS.

C. TOTAL C_o REMOVED.

FIG. No.4.

TEST C42. ELUTION OF Co WITH 35% NH_4CNS AT ROOM TEMP.



for removing the polythionates, silica and sulphur, these solutions had but little effect on the cobalticyanide poisoning.

Attention was therefore directed to the removal of this anion. Experience obtained in earlier work showed that the only promising lines of investigation were variations in the thiocyanate treatment previously established.

The use of hot 50% NH_4CNS was considered neither practicable nor economic. Figure No. 3 shows the effect of the NH_4CNS concentration on the elimination of cobalticyanide under boiling conditions and 16 hours contact time. (Test C41.) This graph shows that if removals of Co exceeding 90% are to be obtained, the minimum concentration of NH_4CNS should be 20%. If more than 95% removal is to be obtained, a concentration of 35% is required. As observed previously, about 10-20% of the cobalt present remained on the resin as a cobalt thiocyanate complex, after the NH_4CNS treatment. In the small scale tests this was removed by oxidation of the CNS' with bromine. This procedure was obviously not practicable on a large scale, but it was shown that efficient oxidation could be achieved by allowing the resin to stand in 30% nitric acid in the cold.

The elution of the poisoned resin in a column with cold NH_4CNS only produced a 22% removal of the cobalticyanide present. The elution curve is illustrated in Figure No. 4. It was hoped that this procedure would bring about better removals since the used NH_4CNS is continuously being replaced. The elution curve however, shows that although fairly high concentrations of cobalt are encountered in the initial fractions of the eluate, this concentration rapidly drops. By measuring the areas under this elution curve at definite volumes, a graph of the cumulative percentage cobalt eluted against the volume of eluting solution, can be obtained. This curve flattens out rapidly and indicates that the maximum amount of cobalticyanide that can be eluted by

reasonable amounts of NH_4CNS is approximately 25%.

Elution of the resin in column form with 35% NH_4CNS at 60°C. gave slightly higher extractions, but as shown in Figure No. 5, a maximum removal of approximately 45% was all that could be expected. This temperature is recommended by the manufacturers as being the maximum safe temperature limit.

It was noteworthy that in the latter two experiments no green colour of the cobalt thiocyanate complex was observed on the resin, as would be the case with boiling solutions.

Other variations of the thiocyanate regeneration were attempted, such as thiocyanate in organic solvents and thiocyanate in alkaline solutions. These showed little promise as regenerants. The highest removal obtained without the use of boiling temperatures was elution with 50% KCNS on the hydroxide form of the resin, when 61% of the cobalt was removed. (Table No. 11).

Investigations into a large number of other eluting agents such as :-

10% $NaNO_2$ in acetic acid.

5% NaOCl, followed by 10% H_2SO_4

NaCN, followed by Na_2S to form CNS on the resin.

$Na_2S_4O_6$.

Zn dust in NaOH.

Dil. HCl and Zn.

NaOH and Al.

$KMnO_4$ in dil. H_2SO_4.

$KMnO_4$ in alkaline solution.

Aqua Regia.

$K_2Cr_2O_7$ in H_2SO_4.

Cuprammonium Hydroxide.

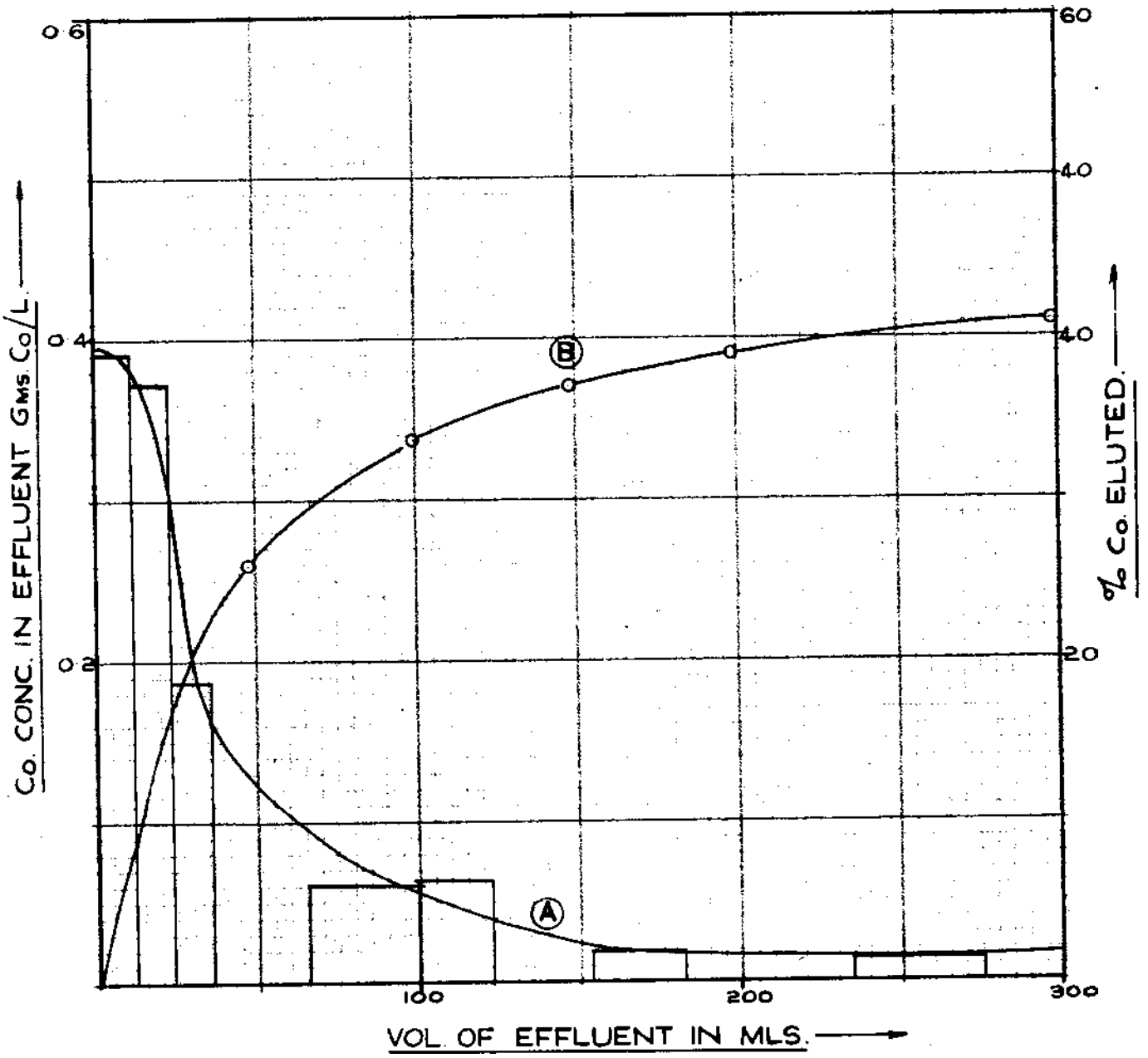
Cuprammonium Cyanide.

Conc. NH_4OH.

TABLE NO. 11

FIG. No. 5.

TEST Co. ELUTION OF Co. WITH 35% NH_4CNS. AT 60°



A. % Co. ELUTED

B. Co IN EFFLUENT.

FIG. No. 5B.

APPARATUS FOR HOT NH_4CNS ELUTION

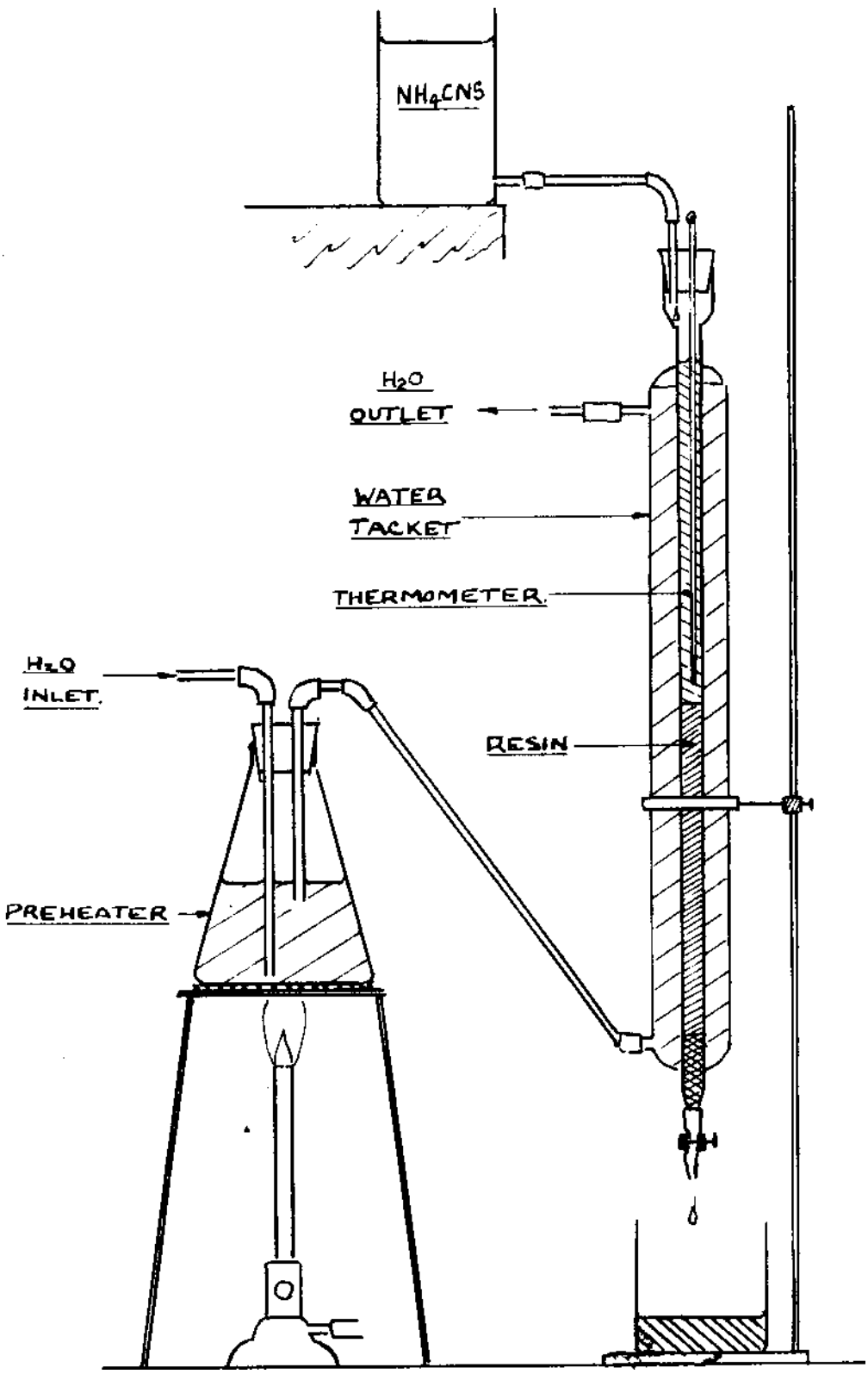


TABLE NIL.

REMOVAL OF COBALTICYANIDE FROM POISONED RESIN BY MEANS OF VARIATIONS OF THE THIOCYANATE METHOD.

NO.	DESCRIPTION OF RESIN USED.	DETAILS OF REGENERATION PROCEDURE	TOTAL Co REMOVED	REMARKS
1.	Western Reefs Poisoned Resin Containing 1.36% Co.	Resin Boiled with 5% w/v NH_4Cl for 1 hour. Allowed to stand overnight for hrs. at 90°C Boiled with Br_2 in HCl.	98%	After NH_4CNS treatment, resin turned bright green, colour removed by Br_2 in HCl.
2.	Western Reefs Poisoned Resin Containing 1.72% Co.	Eluted with 35% NH_4CNS in the cold. ± 200 mls/gram resin.	22%	No green colour on resin after NH_4CNS treatment
3.	Western Reefs Poisoned Resin Containing 1.72% Co.	Eluted with 35% NH_4CNS at 60°C ± 200 mls/gram resin.	42%	No green colour on resin after NH_4CNS treatment
4.	West Rand Cons. Resin from Set 2. 2.40% Co.	Resin Eluted with 50% KCNS at room temperature. 200 ml/gram resin . Followed 20% HNO_3.	28%	No green colour on resin after NH_4CNS treatment
5.	West Rand Cons. Resin from Set 2. 2.40% Co.	Resin converted to $(OH)^1$ form. luted with 5% KCNS. 100 ml/gram resin. llowed by 20% HNO_3	61%	No green colour on resin after NH_4CNS treatment
6.	West Rand Cons. Resin from Set 2. 2.40% Co.	Resin eluted with 5% KCNS in % NaOH 100ml/gram resin. Followed by % HNO_3	39%	No green colour on resin after NH_4CNS treatment
7.	West Rand Cons. Resin from Set 2. 2.40% Co.	Resin eluted with Acetone saturd with NH_4CNS. 100 ml/gram resin. owed by 20% HNO_3	5.6%	Eluate coloured deep orange. Much organic matter present.
8.	West Rand Cons. Resin from Set.2. 2.40% Co.	Resin eluted with Amyl Alcohol turated with NH_4CNS. 100 ml/gram resin.	3.4%	
9.	West Rand Cons. Resin from Set 2. 2.40% Co.	Resin eluted ith Acetone cont ng 5% NaOH, 6% H_2O, saturated ith NH_4CNS. ml/gram resin resin. Followed by 20% HNO_3	35%	Eluate coloured deep orange. Much organic matter present.
10.	West Rand Cons. Resin from Set 2. 2.40% Co.	Resin eluted with EtOH. Satur ith NH_4CNS nd 5% NaOH. 100 ml/gram resi Followed by 20% HNO_3	13%	

were carried out both at the Government Metallurgical Laboratory and Calcined Products (Pty) Ltd., but none of these showed any promise as an efficient means of eliminating the cobalt.

A search for a cheaper regenerant than the 50% NH_4CNS is still in progress, but it must be admitted that there is very little likelihood of one being found. It is significant to note that in a report issued by the Chemical Research Laboratory Great Britain,[131] the adsorbtion of cobalticyanide on Amberlite IRA.400 is described in connection with the recovery of gold using anion exchange resins. It was found that cobalticyanide could be removed from the resin completely and efficiently by means of 2M KCNS in the cold. This elution, however, was carried out almost immediately after adsorbtion had taken place. It appeared probable that the longer the cobalticyanide was allowed to remain on the resin, the more difficult would be its removal.

This was confirmed in an experiment in which Amberlite IRA.400 resin was loaded with a synthetic solution of cobalticyanide. Immediately after adsorbtion all the cobalticyanide on the resin could be removed with 2M KCNS, but after standing for three months, only 86% of the cobalt present could be removed with the same reagent. In this experiment it was also observed that no green colour of the cobalt thiocyanate complex appeared on the resin in the former elution, whereas in the latter the resin assumed a brilliant green colour on the passage of the KCNS.

It appears possible, therefore, that the cobalticyanide anion undergoes some slow reaction whereby it becomes firmly attached to the resin and this fact suggests that a solution to the problem of removing the cobalticyanide will only be obtained after a fundamental study into the reactions of the cobalticyanide anion with the exchange groups on the resin has been undertaken.

In order to make provision for the immediate future it was apparent that the elimination of the cobalticyanide subsequent to its adsorbtion on the resin was not a practicable proposition and that every attempt should be made to eliminate the cobalticyanide from the solutions to be treated.

2. METHODS OF ELIMINATING THE POISONS BEFORE COMING INTO CONTACT WITH THE ION EXCHANGE RESINS.

In view of the difficulty encountered in removing the cobalticyanide anion from the Amberlite IRA.400 resin, experiments were undertaken to determine if it were possible to eliminate this anion before coming into contact with the anion exchange columns.

Most promising of the possibilities appeared to be the thorough washing of the cyanide residue prior to leaching.

Preliminary tests on the uncyanided Western Reefs ore showed that the cobalticyanide was definitely formed during the cyanidation and that the amount appearing in the uranium pregnant solution could be substantially reduced by thorough washing prior to leaching.

In these tests 500 gm. samples of the uncyanided ore were subjected to the normal cyanidation treatment, which was followed by various washing treatments. The washed ore was then leached with sulphuric acid and MnO_2, and the uranium pregnant solution passed through a small column of resin. The resin was then ashed and analysed for cobalt. The results of these experiments are shown in Table No. 12.

62/ TABLE NO. 12

TABLE NO. 12.

EFFECT OF WASHING THE CYANIDE RESIDUE ON COBALTICYANIDE ADSORBTION BY THE RESIN.

DESCRIPTION OF WASHING TREATMENT	Co. adsorbed on the resin
No wash after cyanide filtration.	0.071 mgm.
Cyanide residue washed once with water.	0.057 "
Cyanide residue washed once with water, repulped to 50% solids with water, filtered and washed with water.	0.032 "
Cyanide residue washed with water, repulped to 50% solids with 0.1% H_2SO_4, filtered and washed with 0.1% H_2SO_4.	0.011 "
Cyanide residue washed with water, repulped to 50% solids with barren solution, containing 0.1% free H_2SO_4, filtered and washed with water.	0.027 "

Although these results showed that the cobalticyanide poisoning could be substantially reduced by washing of the cyanide residue, it was appreciated that these tests which were conducted on a laboratory scale were of little use in assessing the practicability of washing as a method to eliminate the cobalticyanide on the full scale plants. It was obvious that the amount of cobalticyanide produced during a single cyanidation treatment was only a fraction of the total amount circulating in the recycled cyanide solutions used in plant practice. Also the washing efficiency obtained using a Buchner suction filter (as was the case in the test described above) could be expected to be considerably higher than that obtainable on an Oliver filter. It was recommended, therefore, that in order to obtain more representative results, washing tests similar to those described above should be undertaken at the Western Reefs Pilot Plant, where conditions closely resembling those to be encount-

63/ ered....

ered on the full scale plants could be obtained.

Before these tests were undertaken, the ion exchange resins on the full scale uranium plant at West Rand Consolidated had been in operation for approximately four months without any precautions to eliminate cobalticyanide poisoning being taken. The sudden realisation of the serious nature of this type of poison brought about immediate concern regarding the removal of the cobalticyanide anion. At the Western Rand Consolidated Plant no provision had been made for washing the cyanide residue prior to leaching, and the installation of another bank of Oliver filters necessary to carry out this step would have necessitated major alterations of the existing Plant layout. Thus attention was immediately focused on other methods of eliminating the cobalticyanide anion. To this end the operational procedure at West Rand Consolidated was considered in more detail, as a result of which another source of cobalticyanide formation was encountered.

Formation of Cobalticyanide During the Leaching Procedure.

Analyses of the various Plant solutions at West Rand Consolidated showed that more cobalticyanide was appearing in the uranium pregnant solution than could be accounted for by the amount remaining in the cyanide residue prior to leaching. Typical analyses showed that:

(a) The pregnant solution contained 20 mgms/litre total Co.

(b) The barren solution after passage through the columns contained 10 mgms/litre total Co. The difference between these two figures can be taken to represent the amount of cobalt present as the cobalticyanide, i.e. 10 mgms/litre.

(c) The recycled gold barren cyanide solution, which was used as a final wash on the residue prior to leaching, contained only 4 mgms/litre as cobalticyanide.

64/ It.....

It was thus apparent that cobalticyanide was being formed during the leaching prodeduce. On consideration of the operational procedure practised at this plant, a possible source of cobalticyanide formation was considered to be as follows:

After the final wash with barren cyanide solution, before leaching, the alkaline residue (containing a considerable amount of cyanide) was repulped with secondary filtrate. This latter solution contained only a small amount of free acid, certainly not sufficient to neutralise the alkalinity. The resulting slurry was pumped into the leaching pachucas, whilst at the same time an addition of manganese dioxide was made. The major portion of the manganese dioxide was obtained from the precipitation and oxidation of the manganese sulphate in the barren solution from the previous leach. This solution contained considerable amounts of cationic cobalt which was precipitated as a hydroxide during the manganese recovery process and thus appeared in the manganese dioxide slurry added to the pachucas. Thus, during the filling of the pachucas, ideal conditions existed for the formation of cobalticyanide by the reaction of the cobalt hydroxide present in the manganese slurry with the residual cyanide remaining in the residue.

Previous tests had indicated that the formation of cobalticyanide did not occur in acid solutions and it appeared likely that there existed a certain pH value above which cobalticyanide formation took place and below which no such formation occurred.

In order to confirm these suppositions, the following tests were carried out :-

(a) A sample of the West Rand Consolidated cyanide residue was thoroughly washed with water to remove all traces of cobalticyanide already present. This residue was then made into a pulp with water and a small amount of NaCN (½ lb/ton) added. To a portion of this pulp a manganese dioxide slurry containing

Co (obtained from the West Rand Consolidated Plant) was added. To the remaining portion fresh 70% MnO_2 containing no cobalt was added and the two mixtures agitated for 15 minutes before the requisite acid addition was made and the normal uranium leach carried out.

Analysis of the pregnant solutions obtained from these leaches showed that the former contained 2.92 mgms Co/litre as cobalticyanide while the latter contained no cobalticyanide. This test showed conclusively that cobalticyanide can be formed from the cobalt contained in the manganese dioxide slurry used on the Plants.

(b) In order to investigate the pH conditions necessary for the formation of cobalticyanide, a similar series of leaches was carried out in which different amounts of the leaching acid were added to the cyanide residue to provide a slurry at different pH values. An excess of sodium cyanide (4 lb/ton) was added to the washed cyanide residue in order to accentuate the cobalticyanide formation. The manganese dioxide, containing cobalt, was obtained from the West Rand Consolidated Plant. The detailed experimental conditions are shown in Table No. 13.

It was found to be impossible to obtain constant pH values over the range 2-6, large variations being observed during agitation. The results show that cobalticyanide formation reaches a maximum at a pH of 6. Above this value the cobalti-cyanide formation drops steadily until, at a pH of 10, it is practically negligible. At a pH value of 2, a small amount of cobalticyanide was formed, but this formation can be readily explained, since in these experiments the washed cyanide residue was agitated with the comparatively concentrated cyanide solution for a period of 1 hour before the addition of the MnO_2 slurry and adjustment of the pH. Under these conditions it is almost certain that a small amount of cobalticyanide would be

TABLE NO. 15.

TABLE NO. 13.

FORMATION OF COBALTICYANIDE DURING MnO_2 ADDITIONS TO WEST RAND CONSOLIDATED CYANIDE RESIDUE

WT. OF ORE (gms)	INITIAL ACID ADDED lbs/ton	pH BEFORE ACID ADDITION	pH AFTER ACID ADDITION	MnO_2 ADDED AS SLURRY lbs/ton	COBALT PRODUCED MnO_2 mgms.	TOTAL ACID ADDED lbs/ton	VOL. PREG. SOLUTION mls.	COBALTICYANIDE IN PREG. SOL. mgm Co/litre.	TOTAL COBALTICYANIDE FORMED mgm Co.	pH AFTER MnO_2 ADDITION
500	0	10.0	10.0	5	2.6	50	395	0.7	0.27	9.8
"	2	"	8.8	"	"	"	380	1.00	0.38	8.9
"	4	"	7.9	"	"	"	435	1.78	0.78	8.2
"	5	"	6.0	"	"	"	440	2.40	1.06	7.6
"	6	"	4.5	"	"	"	415	3.32	1.38	7.1
"	10	"	2.0	"	"	"	360	4.84	1.74	5.9
"	20	"	1.2	"	"	"	380	0.70	0.23	2.0

TABLE NO. 1

EFFECT OF pH ON COBALTICYANIDE FORMATION FROM SOLUTIONS OF $CoSO_4$ AND

COBALT ADDED mgms	NaCN ADDED mgms	pH of $CoSO_4$ SOLUTION	pH OF N SOLUTI	FINAL pH OF MIXTURE	COBALTICYANIDE FORMED mgms Co.
7.65	38.5	2.0	2.0	2.0	0.05
"	"	4.1	4.2	4.1	0.05
"	"	5.3	5.0	5.0	0.30
"	"	7.0	7.0	5.2	0.50
"	"	8.2	8.1	5.3	1.1
"	"	8.6	8.5	6.0	2.8
"	"	8.9	8.9	7.9	3.4
"	"	10.1	10.2	10.8	3.4

FIG. No.6.

FORMATION OF COBALTICYANIDE FROM COBALT IN THE MnO_2 SLURRY & CYANIDE RESIDUE AT DIFFERENT pH VALUES.

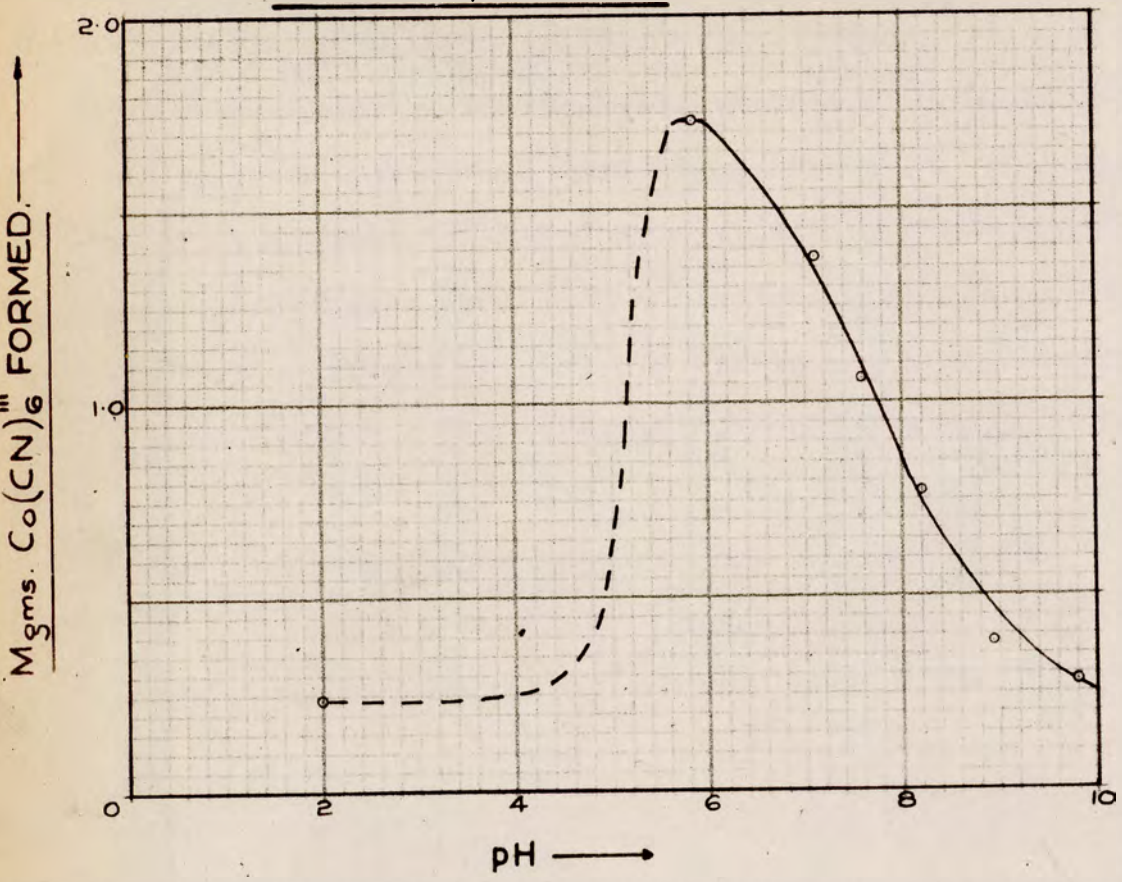
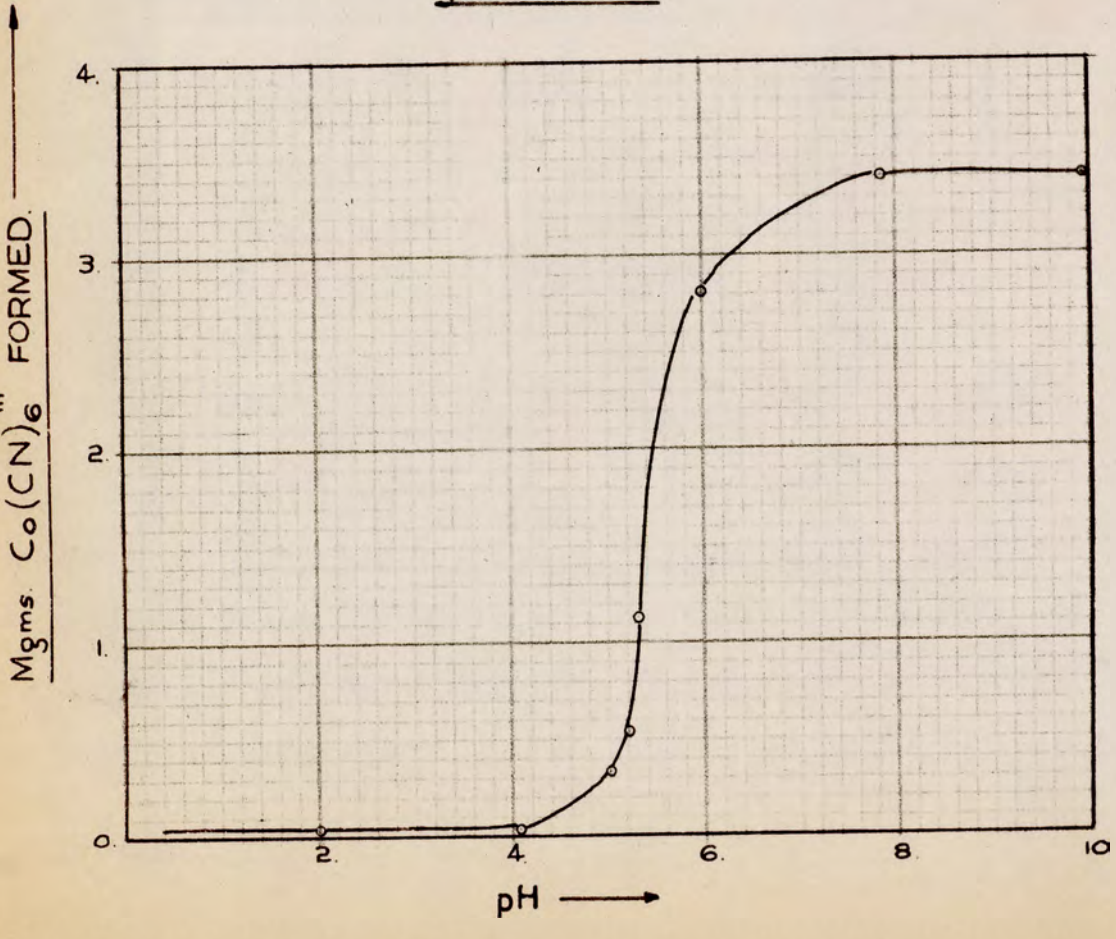


FIG. No.7.

FORMATION OF COBALTICYANIDE IN MIXTURES OF COBALT SULPHATE & SODIUM CYANIDE AT DIFFERENT pH VALUES



formed due to the action of the cyanide on the cobalt in the ore. The results are shown in Table13 and Figure No. 6.

(c) In order to obtain information over the pH range of 2-6 it was necessary to carry out experiments on pure solutions of cobalt sulphate. These solutions were adjusted to various pH values by the additions of NaOH and H_2SO_4. Sodium cyanide, which had previously been adjusted to the same pH value, was then added. The combined pH was then measured, the solutions agitated by means of air blowing and analysed for Cobalticyanide. The results are shown in Table No. 14 and graphically in Figure No. 7.

These results show conclusively that cobalticyanide will not form below a pH value of 4.0

Thus the formation of cobalticyanide could be readily eliminated by the addition of the major portion of the leaching acid to the cyanide residue before any manganese dioxide slurry was added and recommendations to this effect were made to the West Rand Consolidated Plant.

This procedure was then adopted and resulted in a large decrease in the amount of cobalticyanide appearing in the pregnant solution.

Nevertheless the cobalticyanide formed during the actual cyanidation of the ore still presented a major problem and further tests were carried out in an attempt to remove this anion from the pregnant solution.

(3) METHODS FOR ELIMINATING THE COBALTICYANIDE FORMED DURING THE CYANIDATION PROCEDURE.

Several alternatives to the washing of the cyanide residue as a means of eliminating the cobalticyanide were suggested, Investigations were undertaken to study the practicability of these methods at the West Rand Consolidated Plant and Calcined Products (Pty) Limited. Although all these investigations have

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not yet been completed, it is possible to give a brief comparison of the relative advantages of these methods from the results of preliminary tests carried out at the Government Metallurgical Laboratory.

Essentially however, the final choice of the method used will depend on economic considerations and the practical difficulties encountered at the different plants. These are variables which are difficult to study on a laboratory scale and it became apparent that further investigation would result in duplicating work that could be more effectively carried out on the Plants.

1. Precipitation of the Cobalticyanide as an Insoluble Metal Salt by the addition of certain Metals during the Leaching Procedure.

The cobalticyanide anion forms insoluble salts with most of the divalent metals and certain monovalent metals. A descriptive review of the solubilities of the various metallic salts is given by B.S. Evans and D.G. Figgs.[37] These investigators state that the manganese cobalticyanide is insoluble in strong sulphuric acid solutions. In leach solutions, however, it has been found that as much as 10 mgms. of cobalt as $CoCN_6'''$ can be tolerated without precipitation, although approximately 2 gms. Mn^{++}/litre are present. A rough calculation of the solubility product of manganese cobalticyanide shows that under these conditions an exceedingly small solubility product is obtained.

Assuming the above figures of 2.0 gms. Mn/litre and 10 mgms. Co/litre, the following calculation of the solubility product can be made:

$$Mn_3\left\{Co(CN)_6\right\}_2 \rightleftharpoons 3Mn^{++} + 2Co(CN)_6'''$$

Then $S = (Mn^{++})^3 \times (Co(CN)_6)^2$

Where (Mn^{++}) and $(Co(CN)_6)$ represent the molal concentration.

$$S = \left(\frac{2}{55}\right)^3 \times \left(\frac{0.010}{59}\right)^2$$

$$= 7.8 \times 10^{-14}$$

TABLE NO. 15

TABLE NO. 15

PRECIPITATION OF COBALTICYANIDE BY COPPER ADDITIONS TO THE URANIUM LEACH

Weight of Ore.	Cu added			Reagents		Time of Leach	Temp. of Leach	$\{Co(CN)_6\}'''$ in Preg. Soln.	% $\{Co(CN)_6\}'''$ Precipitated in ore.
	Gms Cu^{++}	lb/ton	Added as	lb/ton H_2SO_4	lb/ton MnO_2				
500 gms	0	0	$CuSO_4$	50	5	15 hrs.	30°C.	0.72 mgms	-
500 gms	1	4	"	"	"	"	"	0.14 "	80.6
500 gms	2	8	"	"	"	"	"	0.08 "	88.9
500 gms	3	12	"	"	"	"	"	0.07 "	90.3
500 gms	5	20	"	"	"	"	"	0.12 "	83.3
400 gms	2	10	"	"	"	"	Room Temp. bottle leach	0.03 "	95.7

This result is by no means inconsistent with Evans' and Higgs' assertion. Moreover it shows that in order to reduce the concentration of cobalticyanide to a point where poisoning can be neglected, a metal whose cobalticyanide has a solubility product far below the above value, will have to be found.

The two most promising metals appear to be either silver or copper.[37] The former can be excluded for economic reasons.

Table No. 15 shows the effect of adding copper ions to the acid uranium leach on the amount of cobalticyanide appearing in the pregnant solution. The ore used for these tests was the unwashed cyanide residue from the West Rand Consolidated Plant, and an attempt was made to reproduce plant conditions in respect of temperature, agitation and filtration.

The results show that the cobalticyanide concentration can be reduced to a value of approximately 0.1 mgms/litre by reasonable additions of copper. This value corresponds to an accumulation of 0.05% of Co on the resin every cycle, or complete poisoning of an Amberlite resin in 144 cycles. Thus, this method cannot be considered to provide a complete solution to the problem and suffers from the additional disadvantage of the expense of the copper added, or alternatively the expense and trouble incurred in its recovery, presuming this is possible.

2. The Installation of a Guard Column to Remove the Cobalticyanide Before Reaching the Main Uranium Extraction Columns.

This alternative is being investigated at Calcined Products (Pty) Limited.

It has been found that a weak base anion exchange resin is capable of adsorbing cobalticyanide from synthetic solutions of this anion, and its subsequent removal from the resin can be readily achieved by elution with the solution of ammonium hydroxide and ammonium nitrate.

Provided a similar adsorbtion of cobalticyanide will take

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place from the pregnant solution, this method appears to offer a possible solution to the problem.

3. The Removal of Cobalticyanide Anions From the Recycled Barren Cyanide Solutions.

This alternative is under investigation at the West Rand Consolidated Plant.

A report issued by the Chemical Research Laboratory, Teddington, has shown that the cobalticyanide anion can be effectively removed from the recycled barren cyanide solution by means of Amberlite IRA.400[130,131]. It is apparent that the amount of cobalticyanide formed during each cyanidation procedure is small compared with the total amount of cobalticyanide circulating in the barren cyanide solutions. Thus, if the cobalticyanide formed can be removed before the barren cyanide solution is recycled and used for subsequent cyanidations, or for washing the cyanide residue prior to leaching, the cobalticyanide appearing in the pregnant solution from this source can be virtually eliminated. This method will, of course, only provide a solution if used in conjunction with the recommendations given previously regarding the addition of the manganese dioxide slurry during the leaching procedure.

The method appears to suffer from the following disadvantages:

1. The removal of the cobalticyanide from the resin will present a major difficulty. It is possible, that, provided the thiocyanate elution is carried out before the cobalticyanide has aged on the resin, it will not be necessary to use hot concentrated solutions of this reagent.

2. The strong base anion exchange resin will renove virtually all the excess cyanide ions in the barren solution which partially obviates the advantages obtained in recycling this solution.

70/ 4. The....

4. The Thorough Washing of the Cyanide Residue prior to the Uranium Leach.

The washing of the cyanide residue as a means of eliminating the cobalticyanide anion, although not immediately practical at the West Rand Consolidated Plant, offers the following advantages:

1. Water for repulping and washing is the cheapest reagent available. It is admitted that such a process would require the disposal by the Mines concerned, of a large volume of water containing traces of cyanide. It is considered, however, that the removal of this cyanide would not cause undue trouble, in which case the water could then be used for other purposes.
2. The washing of the ore not only removes cobalticyanide but also thiocyanate, which has been shown to form polythionates, a troublesome, but not serious type of poisoning.
3. During the washing residual cyanide ions will also be removed thus greatly reducing the possibility of the formation of the cobalticyanide during the filling of the pachucas and the addition of the MnO_2 slurry for the uranium leach.
4. The aditional installations for filtration would not be excessive. Acid proof filters would not be required and the filtration rates would be as high as with the unwashed cyanide residue.

APPENDIX - SECTION A.

DETAILED EXPERIMENTAL CONDITIONS AND RESULTS.

Tests C1 - C28

Attempts to Obtain Cobalt Adsorbtion on Anion Exchange Resins by the Addition of Complexing Agents to the Pregnant Solution.

The pregnant solution used for these tests was obtained from the Western Reefs Pilot Plant and was produced by their normal uranium leach. It contained 20.1 mgms/litre total cobalt.

The various complexing compounds were added to this pregnant solution which was then either stirred with approximately 2 gms of resin or passed through a small column of resin. After approximately 16 hours contact time the resin and the solution were separated and each analysed for cobalt.

The compounds added and the results obtained are given in Table No. 16.

Test C30.

Removal of Cobalt with NaOBr.

Approximately 2 gms of Western Reefs poisoned resin were boiled in 100 mls. NaOBr (made by dissolving 10 mls. Br_2 in 100 mls. 15% NaOH and adding HCl until the deep red colour of free bromine just appeared.) The resin was filtered off, washed and analysed for cobalt. The filtrate, together with the washes was also analysed for cobalt.

Original Weight of Resin = 1.91 gms dry RNO_3

Original % cobalt = 1.36

Original % sulphur = 9.0

After Treatment:

Final weight of resin = 1.92 gms. dry RNO_3

Final % cobalt = 1.27

Final % sulphur = Nil. (Eschka's method)

72/ Total....

Total weight of Co in washed = 1.3 mgms.

∴ Co removed $= \frac{0.9}{13.6} \times 100 = 6.6\%$

Test C31.

Removal of Cobalt with HF

Approximately 2 gms of poisoned resin were fumed with 25 ml 40% HF for two hours. The residue was washed with water and eluted with 100 mls. 2 N HCl.

Original Wt. of resin = 1.91 gms dry RNO_3

Original % Cobalt = 1.36

Original % SiO_2 = 2.98

After Treatment:

Final Wt. of resin = 1.81 gms dry RNO_3

Final % Cobalt = 1.17

Final % SiO_2 = Nil

∴ Co removed $= \frac{1.9}{13.6} \times 100 = 14.0\%$

Test C32.

Removal of Cobalt with NaCN

Approximately 2 gms of poisoned resin were stirred with 200 mls 10% NaCN solution. The resin was filtered, washed and analysed for Cobalt:

Original % Co = 1.36

Final % Co = 1.14

∴ Co removed $= \frac{2.2}{13.6} \times 100 = 14.5\%$

Test C33.

Removal of Cobalt with cold 50% NH_4CNS

Approximately 2 gms of poisoned resin were stirred with 200 mls. 50% NH_4CNS solution for eight hours. The resin was filtered, washed and analysed for cobalt.

Original % Co = 1.36

Final % Co = 1.02

TABLE NO. 16.

ADDITIONS MADE TO A PREGNANT SOLUTION TO OBTA

COBALT ADSORBTION

TEST NO.	ADDITIONS MADE TO THE PREGNANT SOLUTION	POSSIBLE COMPOUND FORMED	TEMP	ATCH or OLUMN	Co IN BARREN mgms/l	Co ON RESIN
C1	None	None	room	batch	20.1	nil
C2	20 mls 0.1N NH_4CNS i.e. 6x m-mols Co.	Cobalt Thiocyanate	"	"	19.7	"
C3	2 mls 0.1N NH_4CNS	"	"	"	20.0	"
C4	5 mls 0.1M $Co(CNS)_6$ solution	"	"	"	50.2	"
C5	20 mls 0.1N NH_4CNS	"	"	olumn	20.1	"
C6	SO_2 gas bubbled for 1 hr	Polythionate	"	batch	"	"
C7	SO_2+H_2S bubbled " "	"	"	"	"	"
C8	H_2S bubbled for 1 hour	"	"	"	"	"
C9	Susp. MnO_2+ SO_2 gas	"	"	"	"	"
C10	" " " $+H_2S$ gas	"	"	"	"	"
C11	" " " " "	"	4^oC	"	"	"
C12	Sodium Dithionate	"	"	"	"	"
C13	" Trithionate	"	"	"	"	"
C14	" Tetrathionate	"	"	"	"	"
C15	" Thiosulphate	Unknown Complexes	room	"	"	"
C16	" Persulphate		"	"	"	"
C17	" Sulphite		"	"	"	"
C18	" Sulphide		"	"	"	"
C19	" Bisulphite		"	"	"	"
C20	" Hydrosulphite		"	"	"	"
C21	" Cyanide	Cobalticyanide	"	"	"	"
C22	" Nitrite	Cobaltinitrite	"	"	"	"
C23	" Orthophosphate	Unknown Complexes	"	"	"	"
C24	" Metaphosphate		"	"	"	"
C25	" Pyrophosphate		"	"	"	"
C26	" Fluoride		"	"	"	"
C27	" Silicate		"	"	"	"
C28	" Silicofluoride		"	"	"	"

$\therefore$ Co removed $= \frac{3.4}{13.6} \times 100 = 25.1\%$

Test C34.

Removal of Cobalt with hot 50% NH_4CNS

Approximately 1 gm of poisoned resin was boiled for one hour with 50% NH_4CNS, then allowed to stand on a hot plate for 16 hours. The resin which had assumed a green colour, was then filtered off and washed. The combined filtrate and washings were analysed for cobalt. The resin was then boiled with 10% Br_2 in HCl for one hour, filtered and washed. The filtrate and washings were analysed for cobalt. The resin was ashed and analysed for cobalt.

Original Wt. of Co present on resin	= 13.0 mgms.
Wt. Co in NH_4CNS solution & washes	= 10.5 mgms. (81%)
Wt. Co in Br_2 solution and washes	= 2.3 mgms. (18%)
Total Co removed	= 12.8 mgms. (98%)
Co remaining on resin.	= Trace

Test C35

Qualitative Tests on the NH_4CNS Extract Obtained in C34.

(a) The NH_4CNS extract was boiled with Na_2CO_3 while bubbling CO_2 through the solution. The gasses evolved were passed through a solution of $AgNO_3$. (A test for CN^- in the presence of CNS^-)

A slight, but inconclusive, cloudiness was observed in the $AgNO_3$ solution.

(b) On carefully destroying the CNS^- by the addition of small amounts of conc. HNO_3, followed by repeated evaporations to dryness, a pink precipitate was observed to remain in the solution. On filtering off this precipitate, washing and shaking it with water containing a small amount of NH_4OH, and bubbling H_2S through the suspension, the pink precipitate was replaced byablack precipitate of CoS. After filtration

74/ and.....

and fuming with H_2SO both the filtrate and the precipitate gave positive tests for Co in approximately equal amounts. These results indicate that the pink precipitate is a cobalt cobalticyanide. On the passage of H_2S the cobalt is precipitated as a sulphide liberating cobalticyanic acid, which is decomposed on fuming with H_2SO_4.

$$Co_3\{Co(CN)_6\}_2 + 3S'' = 3\,\underline{CoS} + 2\{Co(CN)_6\}'''$$

and

$$6H^+ + 2\{Co(CN)_6\}''' + 8H_2SO_4 + 13\,H_2O = 2CoSO_4 + 6(NH_4)_2SO_4 + 11CO + CO_2$$

(c) On adding excess $AgNO_3$ to a portion of the thiocyanate extract, a copious white precipitate (mainly AgCNS) is obtained. This precipitate was filtered and washed and the AgCNS destroyed by boiling HNO_3. After repeated additions of HNO_3 a small amount of the white precipitate remained undissolved. This precipitate was found to be soluble in conc. NH_4OH. On fuming this precipitate with H_2SO_4 it dissolved and on dilution gave a positive test for Co. These observations indicate the formation of $Ag_3\{Co(CN)_6\}$, a white precipitate soluble in NH_4OH but insoluble in HNO_3.

Test C36.

Increased Nitrogen Content of the Poisoned Resins.

Six 1 gram samples of finely crushed poisoned resin were weighed out and on three of these the total nitrogen determined by Kjeldahl's method. The remaining samples were treated with NH_4CNS as described in Test C34 and again analysed for total nitrogen. The following results in triplicate analysis were obtained:

	A	B	C
Original Total Nitrogen in millieqivalents/gram	4.26	4.25	4.37
Final Total Nitrogen in millieqivalents/gram	2.88	2.91	2.88
Co removed in NH_4CNS mgms/gm	10.2	10.3	10.4
Co removed in Br_2 washes mgms/gm	2.4	2.1	2.2
Total Co removed mgms/gm	12.6	12.4	13.3
Millimols Co removed	0.214	0.210	0.225
Drop in Total Nitrogen in millieqivalents	1.38	1.35	1.49
Ratio $\frac{\text{Milliequivalents N decrease}}{\text{millimols Co removed}}$	6.44	6.42	6.60

Test C37

Qualitative Tests on the 1N HNO_3 Eluates from Western Reefs Poisoned Resin.

A portion of the eluate was neutralised with Na_2CO_3 (neutral solution)

(a) Neutral Soln. + KOH - No precipitate.

(b) Neutral Soln. + Dil HCl - No precipitate.

(c) Acid Soln. + $AgNO_3$ - Yellow precipitate rapidly turning black

(d) Neutral Soln. + Ammoniacal $AgNO_3$ - No colour in cold but black colouration on warming.

(e) Neutral Soln. + $HgNO_3$ - Yellow precipitate.

(f) Neutral Soln. + $HgCl_2$ - Yellow precipitate on warming.

(g) Neutral Soln. + $KMnO_4$ - Immediate decolouration in cold.

The above reactions are those given by polythionates.

Test C38.

Analysis of Poisoned Resins for Polythionates by Reaction with Na_2SO_3

The sample of poisoned resin was reacted with 50 mls. of a 4 N Na_2SO_3 solution made just alkaline to phenolphthalein with NaOH and saturated with Na_2SO_4. The object of the Na_2SO_4

76/ added.....

added is to obtain a solution of high anionic strength to displace the reaction products from the resin. After removing the resin the excess SO_3'' was rendered inactive by the addition of 5 mls of 40% formaldehyde solution and the solution made acid with 20 mls. 10% acetic acid and titrated immediately with $\frac{N}{10}$ iodine solution to the starch end point.

The resin used contained 7.5% sulphur.

The results are shown in Table No. 17 below.

TABLE NO. 17.

ANALYSIS FOR POLYTHIONATES WITH SO_3'' SOLUTIONS

Reaction Conditions	Titre in mls. 0.1 N I_2 Soln/gm. of resin.
A Resin stirred with 50 mls SO_3'' Soln. in cold for 1 hour	8.65 mls.
B Resin stirred with 50 mls SO_3'' Soln. in cold for 16 hours.	9.8 mls.
C Resin in column eluted with 50 mls cold SO_3'' soln.	11.2 mls.
D Resin boiled with 50 mls SO_3'' Soln. for 1 hour.	10.8) mean 11.7) 11.2 mls.
E Resin boiled with 50 mls SO_3'' Soln. for 2 hours.	10.9) mean 11.3) 11.1 mls.

The general equations for the reactions of polythionates with sulphites is as follows:-

$$S_nO_6'' + (n - 3)\ SO_3'' = S_3O_6'' + (n - 3)\ S_2O_3''$$

$$(n - 3)\ S_2O_3'' + \left(\frac{n - 3}{2}\right) I_2 = \left(\frac{n - 3}{2}\right) S_4O_6'' + (n - 3)I'$$

Whence the % sulphur on the resin is given by

$$\%S = \frac{0.32\ n\ .\ t}{w(n - 3)}$$

Where n = No of sulphur atoms in polythionate S_nO_6

t = Titre in mls. of 0.1 N I_2 Solution.

w = Wt. of resin.

Assuming all the sulphur to be present as a polythionate,

77/ the.....

the value of n can be calculated from

$$\frac{n}{n-3} = \frac{7.5 \times 1}{0.32 \times t}$$

For the 5 values given above the following values of n are obtained :-

A - n = 4.8

B - n = 5.2

C - n = 5.6

D - n = 5.6

E - n = 5.6

Test C39.

Analysis of Poisoned Resins for Polythionates by Reaction with NaOH

Approximately 2 gms. of poisoned resin containing 7.5% sulphur were eluted with 10% NaOH until no further S_2O_3 was detected in the eluate. This eluate was acidified with 10% H_2SO_4, 5 mls. 40% formaldehyde added and the solution titrated with N/10 iodine.

The reactions taking place are :-

$S_6O_6'' \xrightarrow{OH} S_5O_6'' + S$ - A

$2S_5O_6'' + 6OH' = 5S_2O_3'' + 3H_2O$ - B

$4S_4O_6'' + 6OH' = 5S_2O_3'' + 2S_3O_6'' + 3H_2O$ - C

$2S_3O_6'' + 6OH' = 4SO_3'' + S_2O_8'' + 3H_2O$ - D

and combining equations C and D

$2S_4O_6'' + 6OH' = 3S_2O_3'' + 2SO_3'' + 3H_2O$ - E

Thus in the case of the :

Hexathionate S_6O_6, 12 gm. atoms S give 5 gm. mols. S_2O_3.

Pentathionate S_5O_6, 10 " " " " 5 " " "

Tetrathionate S_4O_6, 8 " " " " 3 " " "

Thus the % S can be calculated from :-

$\% S = \frac{t}{w} \times 0.767$ For Hexathionates

$\% S = \frac{t}{w} \times 0.64$ For Pentathionates

$\% S = \frac{t}{w} \times 0.853$ For Tetrathionates

78/ Of.....

Of these formulae only the latter provided agreement between the total sulphur present on the resin and the polythionate as shown in the following table.

TABLE NO. 18.

ANALYSIS OF RESIN FOR POLYTHIONATES WITH NaOH SOLUTION

Weight of Resin	Total mls. N/10 I_2 solution required	% S on resin as S_4O_6	Total % S on resin
2.45	21.1	7.32	7.50
2.90	24.8	7.29	7.50
1.63	14.1	7.35	7.50

Test C40

Total Regeneration Obtainable on Western Reefs Poisoned Resins

Approximately 2 gms of poisoned resin were :-

(a) Fumed with HF to remove all the SiO_2

(b) Boiled with 35% NH_4CNS to remove most of the Co

(c) Boiled with Br_2 in HCl to remove the remaining Co and all the sulphur.

(d) Boiled in water to remove all the excess Bromine.

The chloride capacity of the resin was then determined.

Original Poisoned Resin.

Wt. of resin = 2.66 gms.

% Co = 1.72

% SiO_2 = 5.9

% S = 7.23

Cl capacity = 2.02 millequivalents/gm (56%)

∴ Original Co present = 45.6 mgms.

Co in NH_4CNS = 29.8 "

Co in Br_2 wash = 14.5 "

Total Co removed = 44.3 " (97%)

All S and SiO_2 removed.

Final Cl capacity = 3.75 millequivalents/gm. (104%)

79/ Test C41.

Test C41.

Effect of NH_4CNS Concentration on the Removal of Cobalt from Poisoned Resins

Six 1 gram samples of Western Reefs poisoned resin containing 1.3% of cobalt were boiled with different concentrations of NH_4CNS for 1 hour, and then allowed to stand on a hot plate for 16 hours. The NH_4CNS solution was then filtered off, the resin washed and the solution and the washes analysed for cobalt. The resins were then boiled with Br_2 and HCl and the cobalt removed by this treatment determined by analysis of the Br_2 filtrate.

The results are shown in Table No 19 and graphically in Figure No. 3.

TABLE NO. 19.

EFFECT OF NH_4CNS CONCENTRATION ON COBALT REMOVAL

Conc of NH_4CNS	Vol. of NH_4CNS	COBALT REMOVED IN NH_4CNS		Br_2 wash		Total	
		Wt. mgms	% removed	Wt. mgms	% removed	Wt. mgms	% removed
10%	100 ml	8.88	68.4	0.98	7.5	9.86	75
20%	" "	10.12	78	1.80	13.8	11.92	91.6
30%	" "	10.48	80.5	1.76	13.5	12.24	94.1
40%	" "	10.56	81.2	2.12	16.3	12.68	97.4
50%	" "	10.52	81.1	2.32	17.8	12.84	98.8
50%	5 "	7.44	57.2	2.52	19.4	9.96	76.7

Test C42.

Elution of Poisoned Resin in a Column With 35% NH_4CNS at Room Temperature

8.25 grams of poisoned Western Reefs resin containing 1.36%Co were placed in a column and eluted with 35% NH_4CNS at room temperature :-

80/ Cross.....

Cross sectional area of Column = 0.80 sq. cms.

Resin volume = 19.2 mls.

Resin height = 21.6 cms.

Flow rate = 0.75 mls/minute.

TABLE NO 20.

ELUTION OF RESIN WITH 35% NH_4CNS

Vol Throughput in mls.	Vol. of Sample in mls.	Co in sample gms/litre
24.5	24.5	0.223
49.0	24.5	0.157
72.0	23.0	0.086
145.9	23.9	0.041
229.4	23.5	0.028
322.0	24.1	0.020
413.0	30.0	0.015
813.0	400	0.012
836.0	23.0	0.004

These results are shown graphically in Figure No. 4.

By measuring the area under the elution curve plotted from these figures, the weight of cobalt eluted at given volumes was calculated as shown below:-

TABLE NO. 21.

ELUTION OF COBALT WITH 35% NH_4CNS

VOLUME	WT. Co. ELUTED	% Co ELUTED
24.5	5.47 mgms	4.9
49	9.31 "	8.3
72	11.29 "	10.5
200	17.09 "	16.0
400	21.39 "	19.1
700	24.74 "	22.0

Test C43.

Elution of Poisoned Resin with 35% NH_4CNS at 60°C.

Approximately 3 grams of Western Reefs poisoned resin containing 1.72% Cobalt were placed in a column surrounded by a hot water Jacket (See Figure No.5_B). The resin was eluted with 35% NH_4CNS, the temperature just above the resin bed being maintained between 50°C and 60°C.

Resin Height = 5.1 cms.

Cross sectional area = 1.0 sq. cms.

Weight of resin = 3.12 gms.

Flow rate = 0.75 mls/minute.

By measuring the area under the elution curve plotted from an analysis of the eluate (Figure No. 5), the weight of cobalt removed from the resin at given volumes was calculated as shown below in Tables Nos. 22 and 23.

TABLE NO. 22.

ELUTION OF POISONED RESIN WITH 35% NH_4CNS AT 60°C.

Vol Throughput mls.	Vol. of Sample mls.	Co conc. in sample gms/litre
13.8	13.8	0.382
24.8	11.0	0.371
37.3	12.5	0.188
66.8	29.5	-
96.0	29.2	0.06
118.5	22.5	0.063
151.5	33.0	-
185.5	34.6	0.019
241.1	56.0	-
277.9	36.8	0.015

82/ TABLE NO. 23

TABLE NO. 23.

ELUTION OF POISONED RESIN WITH 35% NH_4CNS AT 60°C

Vol. of Eluate	Wt. Co Eluted	% Co Eluted
50 mls	13.9 mgms	26.0
100 "	18.4 "	34.4
150 "	20.0 "	37.3
200 "	20.8 "	39.1
300 "	22.3 "	41.7

83/ SUMMARY....

SUMMARY AND CONCLUSIONS

The results obtained in the investigation into the nature of the poisons on the resins can be summarised as follows, and the following conclusions drawn :

1. The resins suffer a decrease in capacity due to the chemical poisoning by tetrathionate and cobalticyanide anions. Of these two compounds the former can be readily removed by regeneration with 30% NaOH or 5% Na_2S, whereas the latter is exceedingly difficult to remove and as yet no economic method of regeneration has been found. Thus the tetrathionate poisoning cannot be considered to be a limiting factor in the life of the resins, but the cobalticyanide poisoning, being difficult to remove, must be considered as a major limiting factor in the life of these resins. The presence of 1 mgm. Co/l. as cobalticyanide will bring about complete poisoning in approximately 360 cycles. (This figure refers to Amberlite resin operating on a solution containing 0.5 gms U_3O_8/litre with 0.10 gms U_3O_8 being adsorbed on 1gm resin per cycle.) Thus the life of the resins at Western Reefs and West Rand Consolidated Uranium Plants depends on the extent to which the cobalticyanide concentration in the pregnant solution can be reduced.

2. Physical poisoning of the resin occurs when a resin containing tetrathionates is allowed to stand. The tetrathionates decompose and precipitate sulphur inside the resin, thus bringing about a mechanical blocking of the ion exchange centers. Care should, therefore, be taken to ensure that a resin containing tetrathionate anions should not be allowed to stand in this condition.

3. The presence of both the tetrathionate and the cobalticyanide anions in the pregnant solution is derived from compounds formed during the cyanidation of the ore for gold extraction. Cobalti-

34/ cyanide....

cyanide anions are also formed during the leaching procedure when a recycled manganese dioxide slurry containing cobalt is added to an alkaline cyanide residue containing free cyanide, prior to the addition of acid.

4. Several methods of eliminating these poisons from the pregnant solution have been suggested. The final choice will depend on economic considerations and the results of experiments being carried out at other research centres and on the Plants themselves. The most promising method appears to be the thorough washing of the cyanide residue prior to leaching, which removes simultaneously the cobalticyanide, the thiocyanate (which forms polythionates) and the free cyanide.

S E C T I O N B

INVESTIGATIONS INTO THE LIFE OF VARIOUS ANION EXCHANGE RESINS OPERATING ON THE BLYVOORUITZICHT PREGNANT SOLUTIONS.

INVESTIGATIONS INTO THE LIFE OF VARIOUS ANION EXCHANGE RESINS OPERATING ON THE BLYVOORUITZICHT PREGNANT SOLUTIONS.

PART I.

FIRST LIFE TEST ON AMBERLITE IRA. 400 AND DOWEX I RESINS.

1. INTRODUCTION:

At the end of 1950 sufficient experimental work had been carried out in the United States and South Africa to indicate that efficient extraction of uranium from the Rand Leach liquors could be obtained by the use of anion exchange resins. These early tests indicated that these resins were liable to suffer a decrease in their exchange capacity after only a few cycles operation.[127] In addition, the physical stability of the resins was subject to some doubt, particularly since they were operating on solutions with high ionic strength.

It was therefore considered essential to subject the two anion exchange resins then available, namely the Amberlite IRA.400 (manufactured by Rohm & Haas Co.) and Dowex I (manufactured by the Dow Chemical Co.) to a life test whereby a complete study of the poisoning and disintegration liable to occur could be made. It was considered that conclusive data could only be obtained by subjecting these resins to loading and elution operations closely resembling the procedure to be used in the full scale plants.

An instrument had been designed and made in the United States which would permit automatic control of such a sequence of operations. This "life Tester" was installed at the Government Metallurgical Laboratory and put into use to test the life of the two resins mentioned above.

A full description of this instrument and its method of operation is given in an appendix at the end of this chapter.

At this early stage it was decided to transport the com-

paratively large amount of pregnant solution required for this investigation from one of the two Pilot plants in operation. There appeared to be little to choose between the Western Reefs and Blyvooruitzicht Pilot Plants. The preliminary tests had shown that the pregnant solution produced at Blyvooruitzicht showed the worst loading characteristics[140,141] which suggested that the poisoning of the resin would be more severe on this solution. On this account it was decided to operate the Life tester on the pregnant solution produced at the Blyvooruitzicht Pilot Plant.

2. EXPERIMENTAL CONDITIONS AND RESULTS AFTER 100 CYCLES OPERATION.

The two resins under test were wet screened, the minus 20 plus 60 mesh fraction being used in these tests.

150 mls. of the resin were introduced into 1" diameter glass columns, the heights and volumes of the resin beds being as follows :

	Amberlite IRA.400	Dowex I
Diameter of Column	2.54 cms	2.54 cms
Height of column	29.6 "	29.6 "
Volume of resin	150 mls	150 mls
Weight of resin	46.5 gms	45.4 gms

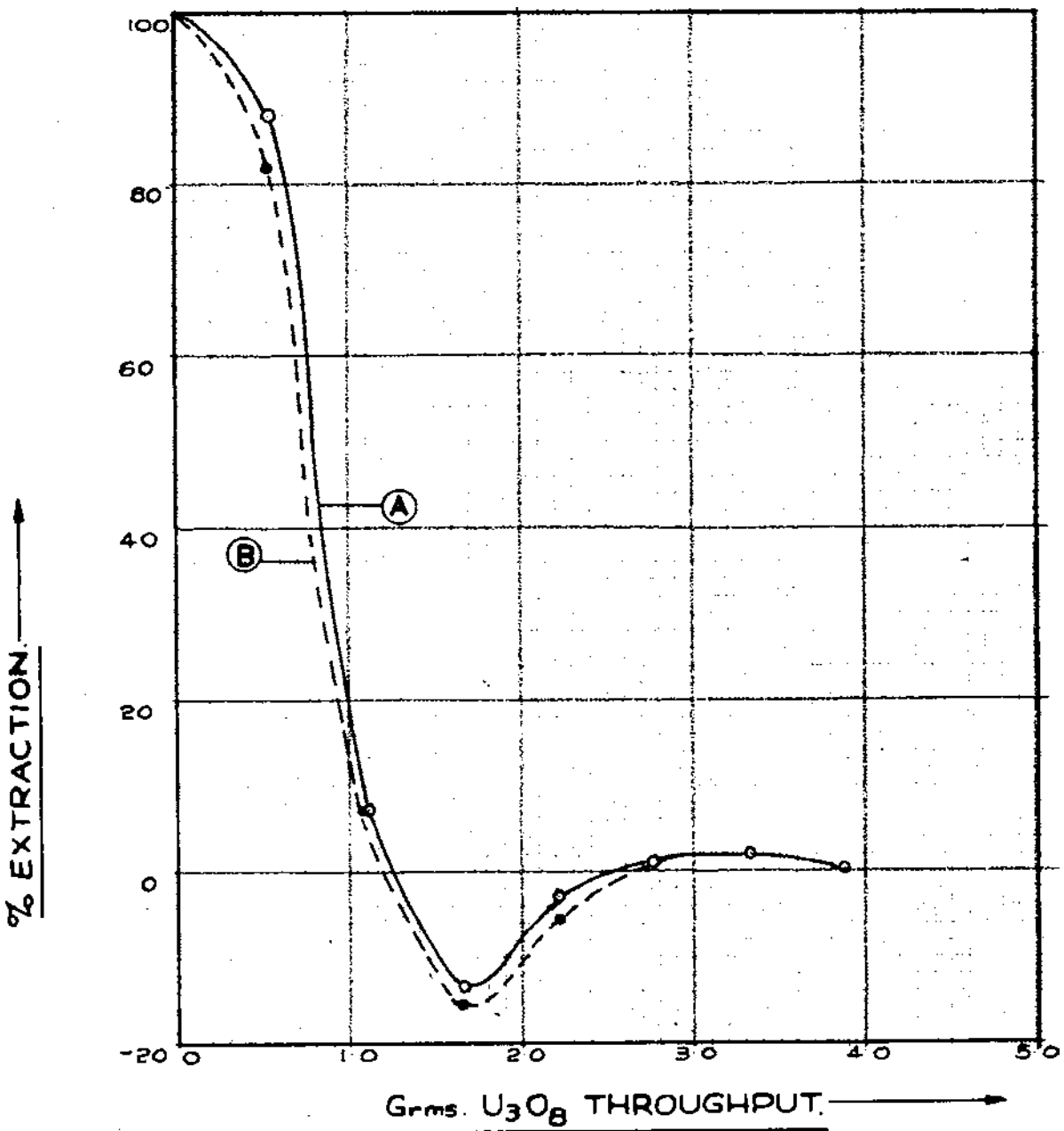
Preliminary Tests:

The initial chloride capacities of the columns were as follows :-

	Amberlite IRA.400	Dowex I
Chloride capacity of whole column in milliequivalents of Chloride ion	158	115
Chloride capacity of resins in milliequivalents Cl/gm. dry RCl	3.35	2.53

FIG No 8

EFFECT OF TEMPERATURE ON THE ADSORPTION OF URANIUM



A. —— 20°C.

B. —— 39°C.

FLOW RATE 66 MLS/MIN

AMBERLITE COLUMN.

A preliminary test was carried out to determine the effect of temperature on the loading characteristics of the resin. Figure No. 8 shows the loading curve obtained at 20°C and 39°C From the small difference between these two curves it can be concluded that minor variations in temperature can be neglected in future work.

Operation of the Life Tester over the 1st 100 cycles.

During this period one complete cycle consisted of :

Adsorbtion @ 60 ml/min	-	2 hrs.
Downwash @ 60 "	-	6 mins.
Elution @ 15 "	-	4 hrs.
Downwash @ 60 "	-	12 mins.

In addition to these operations the columns were backwashed manually each day to eliminate insoluble material consisting mainly of silica which had accumulated in the column.

The pregnant solution used during this period was produced at the Blyvooruitzicht Pilot Plant by their standard leach, no magnetic separation of iron from the cyanide residue prior to leaching being included.

The average analysis of this solution during this period was as follows :

Iron as Fe^{+++}	-	5.0 gms/l.
Uranium as U_3O_8	-	0.25 "
Free H_2SO_4	-	4.0 "
Total sulphate	-	40 "
pH	-	0.9

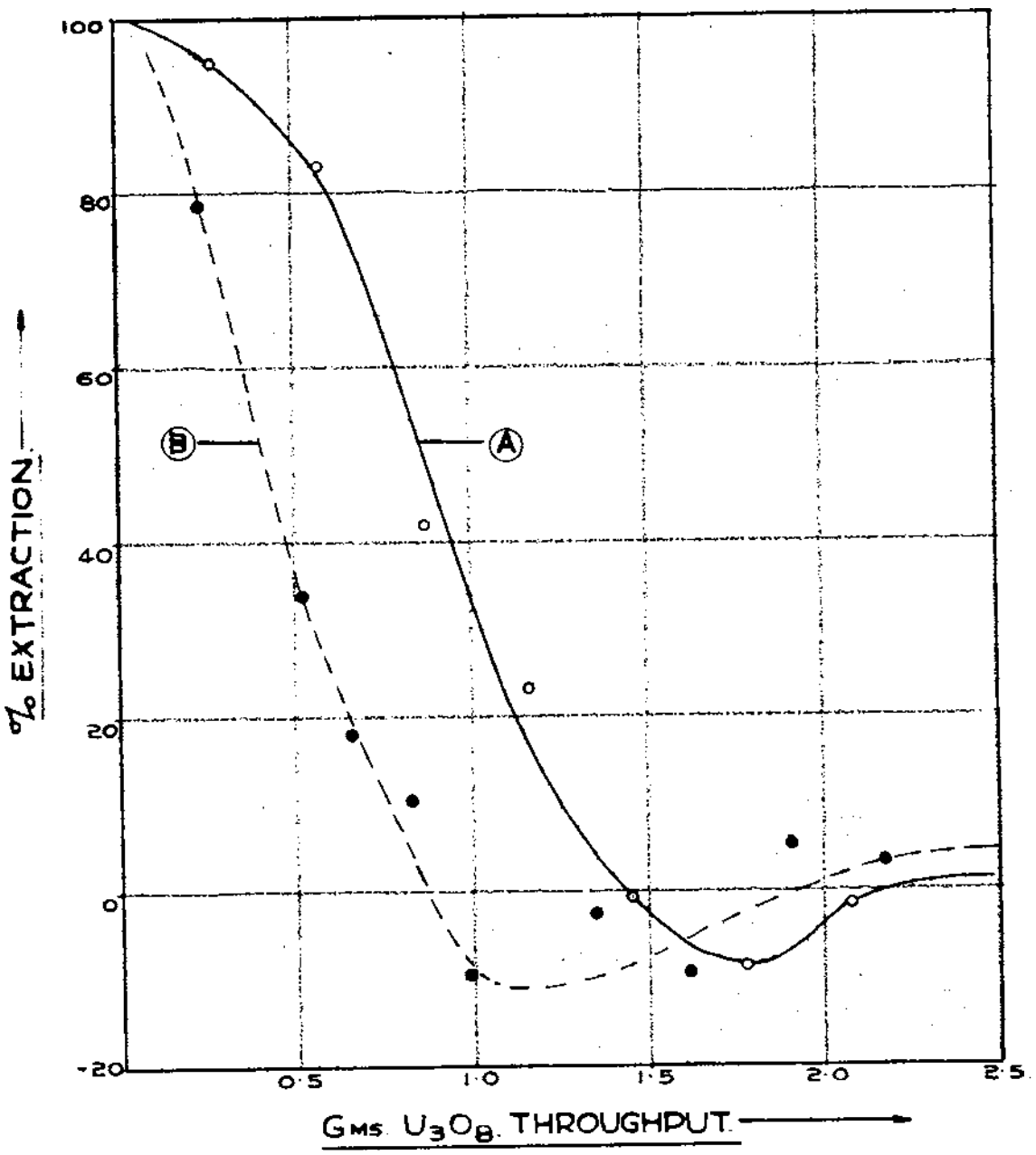
This pregnant solution was clarified in a sand clarifier before being pumped into the Life Tester storage drum. It was noticed, however, that on standing a fine colloidal precipitate occurred in this solution consisting of silica and a small proportion of sulphur.

No attempt was made to obtain maximum uranium recovery.

88/ Each.....

FIG. No 9

INITIAL & 100 CYCLE LOADING CURVES ON AMBERLITE COLUMN.



A. INITIAL LOADING CURVE

U_3O_8 CONC – 0·264 GMS/LITRE

B FINAL LOADING CURVE.

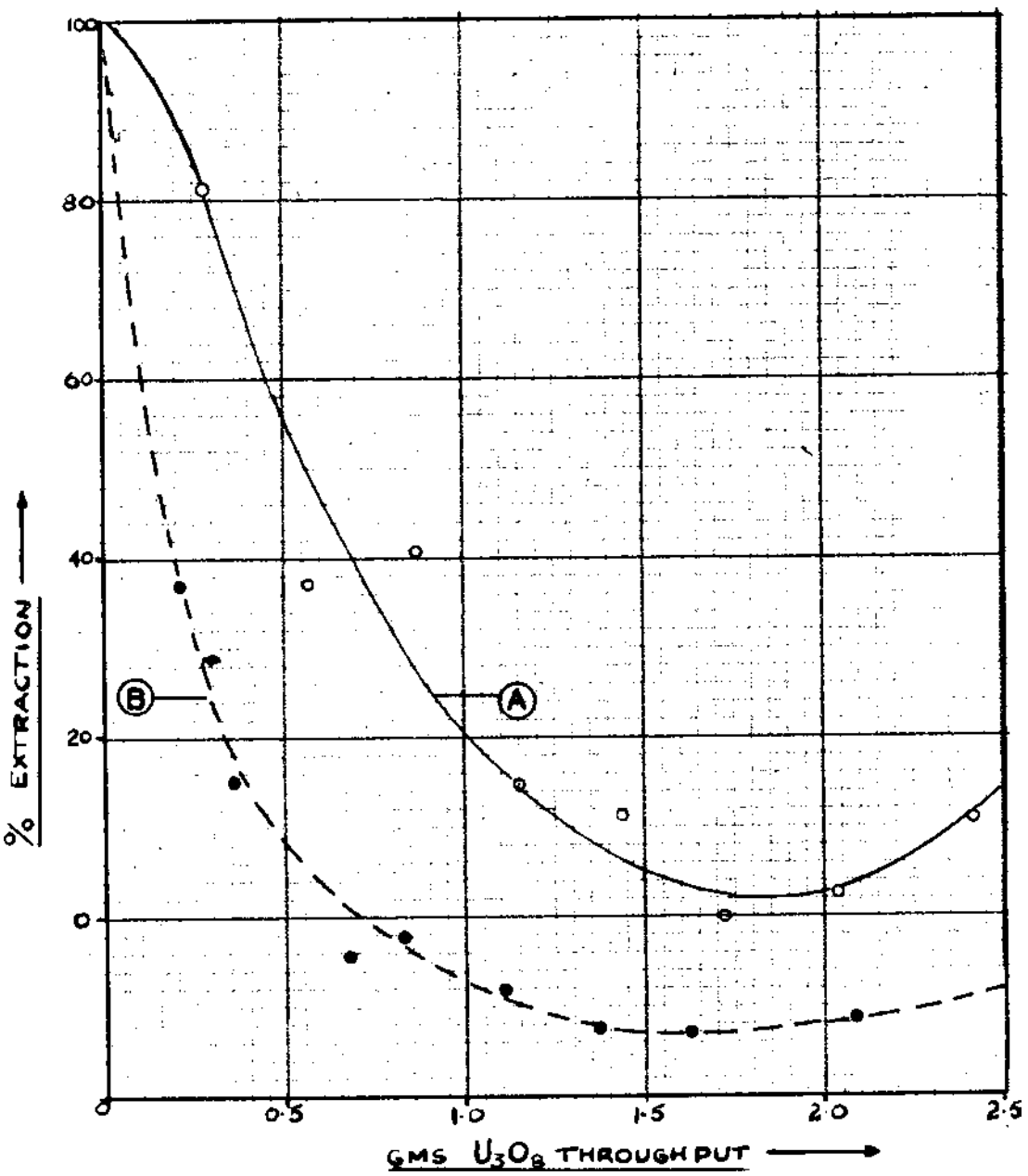
U_3O_8 CONC – 0·242 GMS/LITRE

FLOW RATE 66 mls/min

FIG. No. 10

INITIAL & 100 CYCLE LOADING CURVES

DOWEX COLUMN.



A Initial loading curve:

U_3O_8 CONC. — 0·264 GMS/LITRE

B 100 Cycles loading curve

U_3O_8 CONC — 0·242 GMS/LITRE

FLOW RATE 66 ML8./MIN.

Each column was loaded to saturation at each cycle, and this meant that a large proportion of uranium in the pregnant solution was discarded in the barren solution.

The eluate containing uranium and iron was precipitated with Ammonium Hydroxide to a pH of 6.8, filtered, and the barren eluate acidified and returned to the eluting solution storage drum. This operation was carried out approximately every 20 cycles, i.e. when 25 gals. of eluate and washes had been collected.

Results after 100 cycles:

The chloride capacities of the two columns after 100 cycles operation are given below :-

	Amberlite IRA.400	Dowex I
Chloride capacity of column after 100 cycles, in milli-equivalents Cl^1	136	106
Percentage of fresh resins capacity	87%	92%

The loading curves after 100 cycles together with the initial loading curves are shown in Figures Nos. 9 and 10.

By estimating the areas under these curves, the following amounts of uranium adsorbed were determined.

	Amberlite IRA.400	Dowex I
Uranium adsorbed on column 0 cycles, in gms. U_3O_8	0.78	0.48
Uranium adsorbed on column 100 cycles, in gms U_3O_8	0.44	0.24
Decrease in uranium capacity % fresh resins capacity	44	50

It can be seen that although the chloride capacities had shown only a slight decrease, the amount of uranium adsorbed from a pregnant solution had dropped to about half its original value.

It was noted that these loading curves exhibited the

phenomena of what may be termed "self elution". By this is meant that the uranium concentration in the effluent from the column reaches a value higher than that in the pregnant influent. Consideration of this phenomena led to the conclusion that the uranium already adsorbed was being displaced by some other anion with a stronger affinity for the resin.

At this stage of investigation, however, insufficient experience of the ion exchange adsorbtion characteristics of the various pregnant solutions had been obtained to decide whether these loading curves exhibited exceptionally poor loading characteristics. For comparison purposes a loading curve test was carried out on the Amberlite column using a solution containing only uranium and sulphate ions at the same concentrations encountered in the pregnant solutions. A similar curve was obtained on a fresh resin column of the same dimensions. These two curves are shown in Figure No. 12, and show that only a small fraction of the total uranium capable of being adsorbed under ideal conditions was being extracted from the pregnant solutions. Moreover, the uranium adsorbed from the pure solution by the fresh and 100 cycle Amberlite columns was in approximately the same ratio as the chloride capacities.

Uranium adsorbed by fresh Amberlite column = 6.28 gms U_3O_8

Uranium adsorbed by 100 cycles Amberlite column = 5.65 gms U_3O_8

$\therefore$ % capacity of 100 cycles column = 90

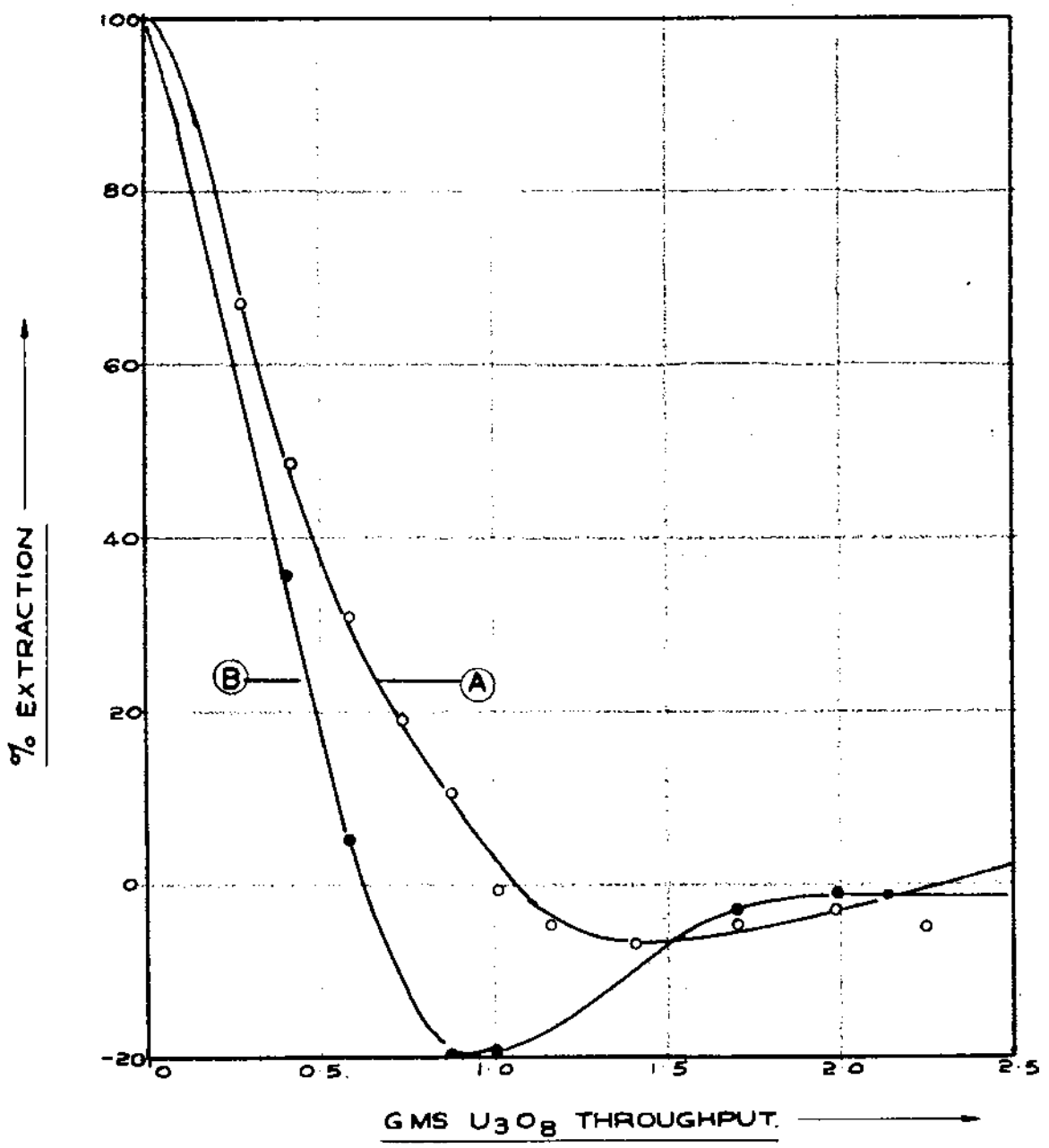
It was therefore apparent that the pregnant solutions used for these tests contained some anion which was being adsorbed preferentially to the uranium. A brief qualitative analysis of the eluate obtained from such a pregnant solution failed to show the presence of any impurity other than Fe^{+++}, $SO_4^{"}$ and silica.

Regeneration Tests:

In view of the decreased capacity of the columns, they

FIG No 11

LOADING CURVES AFTER 6N. HCl. REGENERATION AMBERLITE & DOWEX COLUMNS 101 CYCLES.



A. AMBERLITE

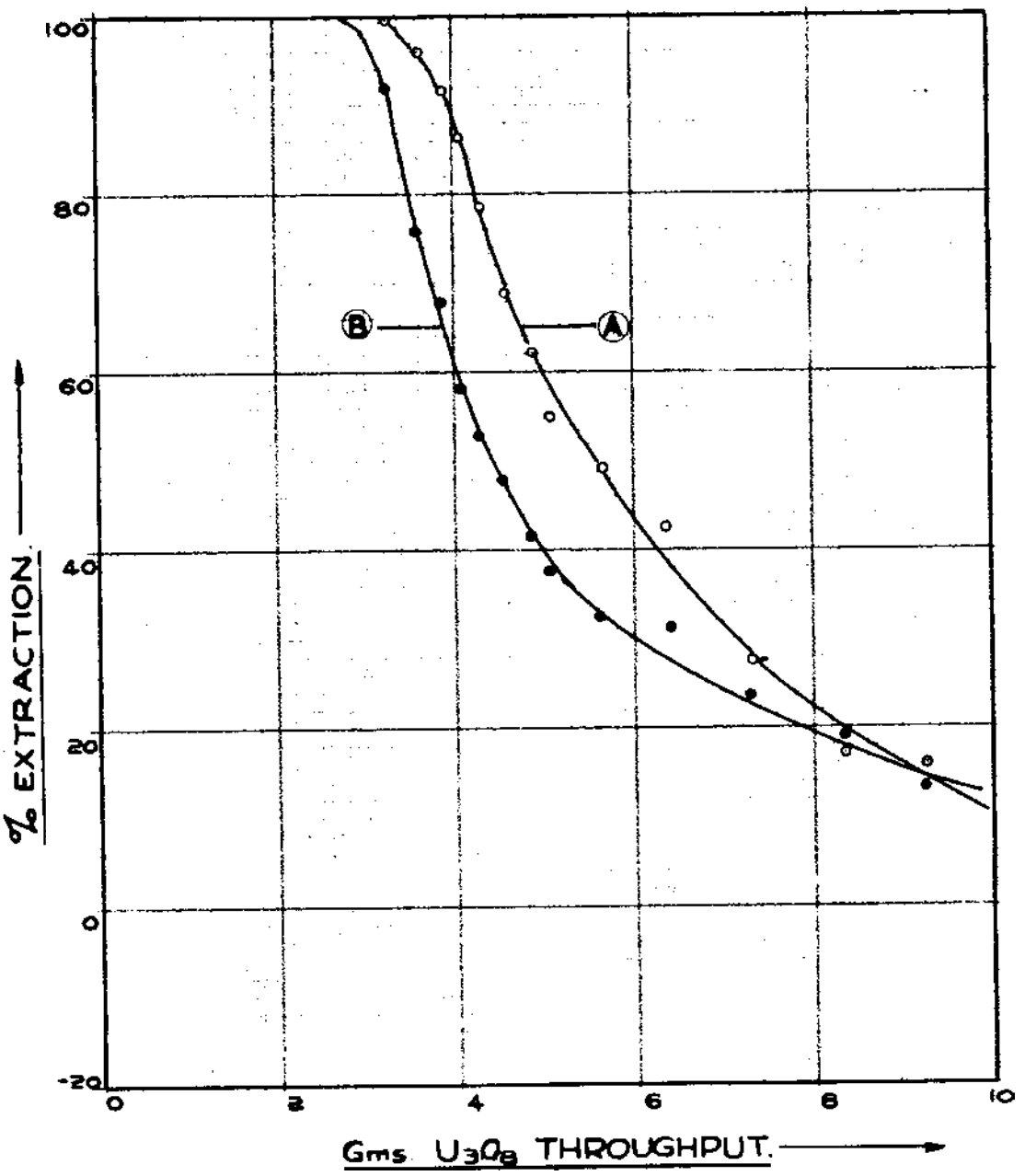
B. DOWEX.

FLOW RATE = 66 Mls/Min

U_3O_8 CONC = 0·247 g/L.

FIG. No. 12.

LOADING CURVES ON AMBERLITE COLUMNS
PURE SYNTHETIC URANIUM SOLUTION.



A. FRESH RESIN

B. 102 CYCLES RESIN.

FLOW RATE 66 Mls/Min.

U_3O_8 CONC. 0·25 Gms/LITRE

were subject to a 6N HCl wash. This procedure was suggested by Mr. Olsen (of the Dow Chemical Co. USA) as a usually effective regeneration procedure. The loading curves obtained after this regeneration shown in Figure No 11 were however virtually identical with the previous curves and showed that no appreciable regeneration had taken place. Other methods of regeneration were not attempted as it was considered that (a) the resins were not seriously poisoned; the uranium capacities calculated from the pregnant solution loading curves giving a false impression of the extent of poisoning due to the exceptionally poor loading characteristics of these solutions. (b) It would be advisable to subject the columns to a further number of cycles in order to obtain a greater accumulation of poisons on the resins so that their identification could be more readily achieved.

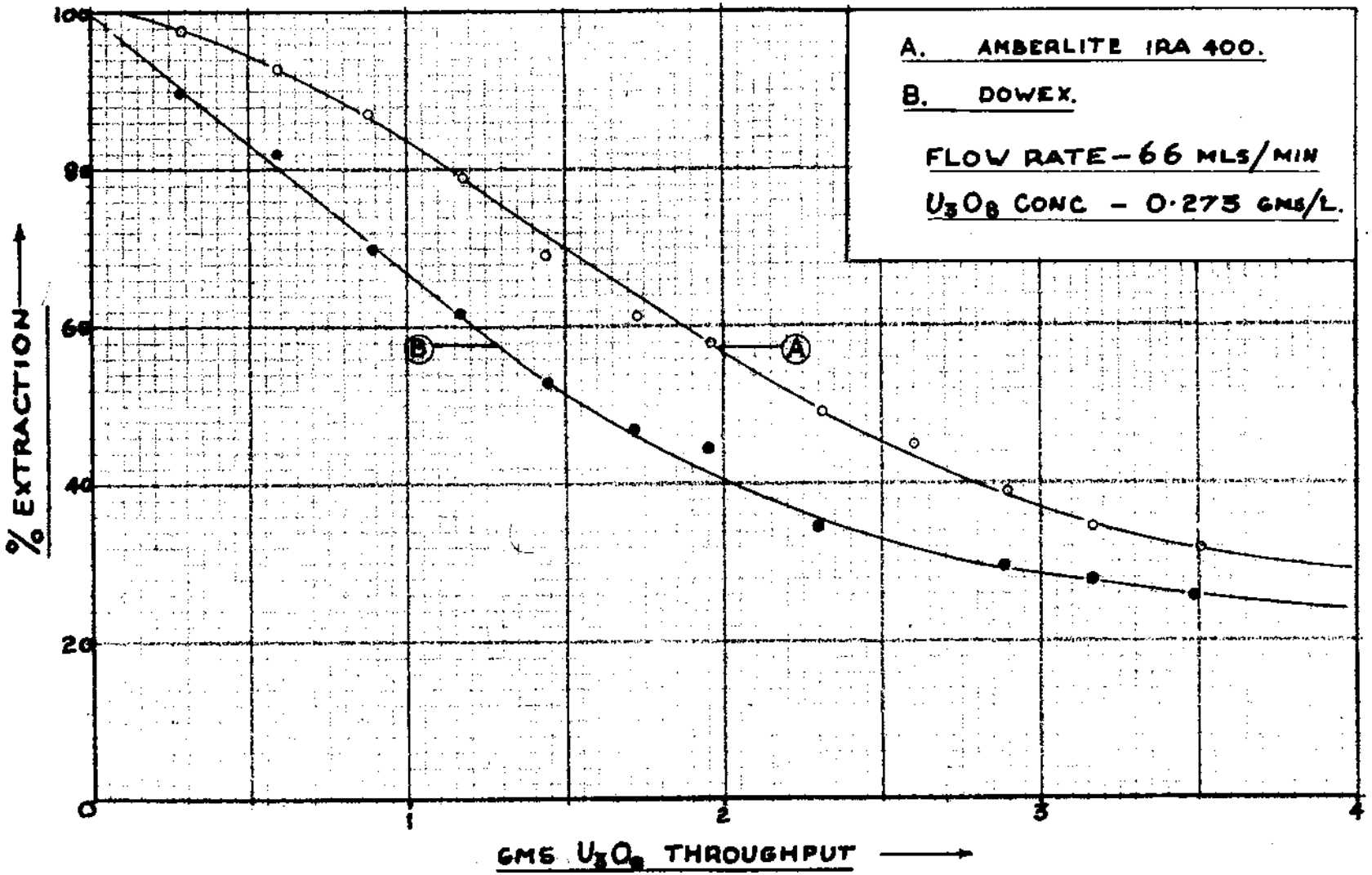
For these reasons it was decided to continue with the Life Test.

3. RESULTS OF THE LIFE TEST OF AMBERLITE IRA.400 AND DOWEX 1 RESINS UP TO 600 CYCLES.

During the period from 100 to 600 cycles a wide variety of pregnant solutions was obtained from the Blyvooruitzicht Pilot Plant. The nature of the work carried out at this Pilot Plant where different leaching procedures were being investigated, resulted in the production of pregnant solutions of widely differing composition. It was impracticable and also inadvisable to store sufficient quantities of pregnant solution to operate the Life Tester for even 100 cycles, so that the loading curves obtained after these periods had to be determined on the pregnant solution being produced at Blyvooruitzicht at that time. This procedure made a comparison of the performance of the resins obtained from data from the loading curves on pregnant solutions almost impossible. During the normal operation

FIG No 13

LOADING CURVES ON AMBERLITE & DOWEX COLUMNS
200 CYCLES.



the adsorbtion time cycle for each particular batch of pregnant solution was adjusted so that the effluent at the end of the adsorbtion period contained 60% of the uranium concentration in the influent. Lower values than this required excessively large amounts of solution due to the flattening out of the loading curve at approximately this 40% extraction level.

The loading curves obtained during the 100-600 cycles period are shown in Figures Nos. 13 - 17, and a brief description of the pregnant solution from which they were obtained is given below:

Loading Curves Obtained at 200 Cycles.

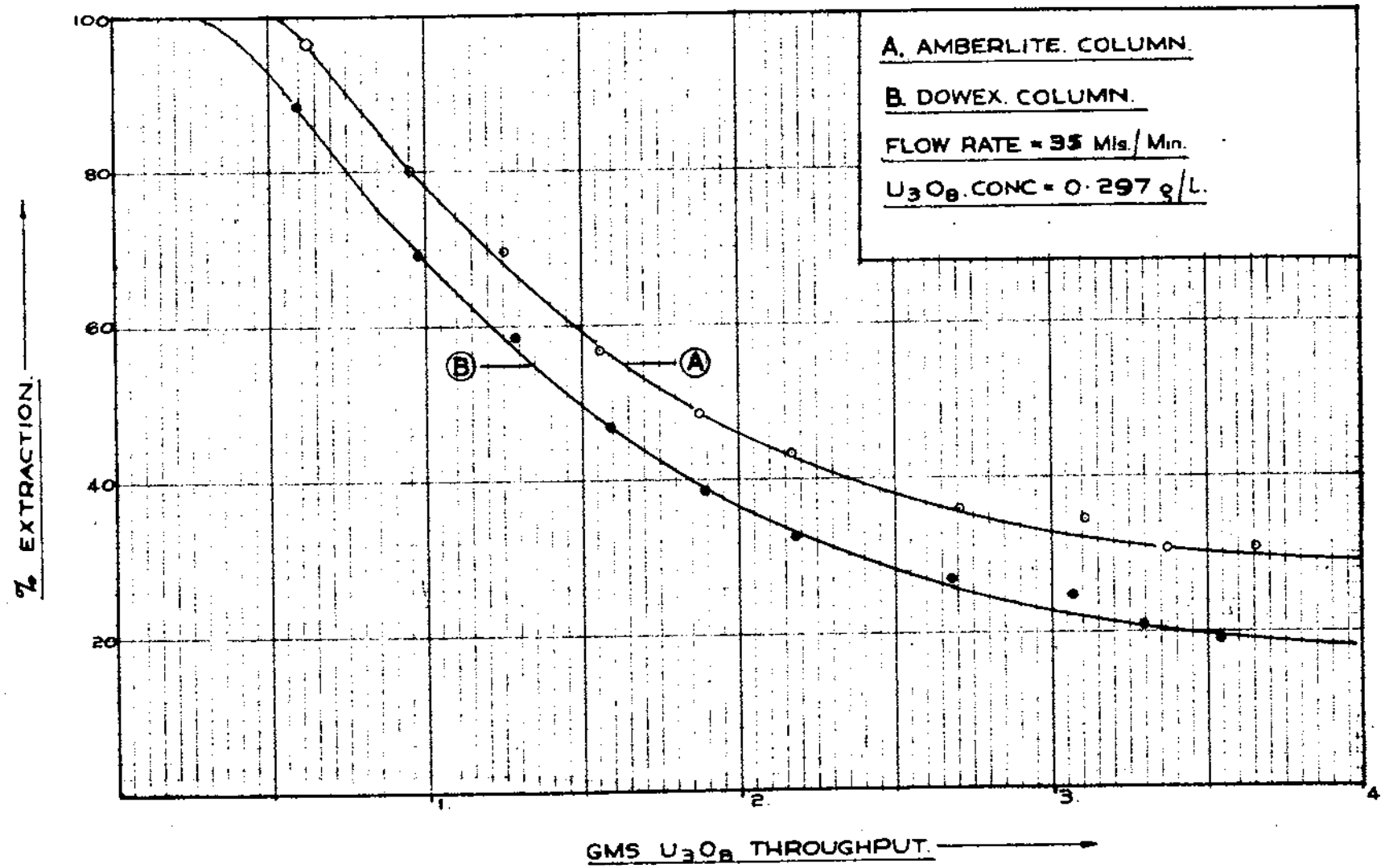
The loading curves obtained at 200 cycles on the Amberlite and Dowex columns are shown in Figure No. 13. These curves show a very marked improvement in the adsorbtion characteristics of the pregnant solution used for this test compared with that used for the 100 cycle test (Cf. Figure No 11). The self elution effect so prominent in the initial and 100 cycle tests was absent, and this points to elimination of the particular ion which was preferentially adsorbed in this latter solution. A comparison of the analyses of these solutions for Fe^{+++} and SO_4'' (which were originally believed to provide the major competition to uranium for adsorbtion on the resin) showed only minor differences in the concentration of these ions. It is thus improbable that the marked improvement in the loading characteristics of this new pregnant solution can be attributed to changes in the Fe^{+++} or SO_4'' concentration.

Composition of Pregnant Solution

	(a) 0 cycles	(b) 200 cycles.
U_3O_8 gms/l	0.264	0.270
Fe^{+++} "	5.4	4.8
SO_4 "	25	40
pH	0.9	1.0

FIG No 14

LOADING CURVES ON AMBERLITE & DOWEX COLUMNS
308 CYCLES.



The improvement became evident when a new batch of pregnant solution was received at 185 cycles. Subsequent enquiries at the Klyvoorultzicht Pilot Plant provided no reasonable explanation, it being stated that no fundamental change had been made in the leaching procedure, the only modification introduced being an improvement in the magnetic separation of metallic iron from the cyanide residue prior to leaching.

A possible explanation for the poor adsorbtion properties of the solutions used for the 0 and 100 cycle tests was only apparent at a much later stage in the investigation, when a more thorough understanding of the nature of the poisons occurring in the pregnant solution had been obtained and this will be discussed in more detail at a later stage.

As will be seen none of the pregnant solutions subsequently received from the Klyvoorultzicht Pilot Plant showed similarly poor loading properties.

Loading Curves Obtained at 308 Cycles.

The loading curves obtained after 308 cycles are shown in Figure No 14. These were observed to be very similar to those obtained in the 200 cycle test. The composition of the pregnant solution used for these tests is as follows:

U_3O_8 concentration - 0.292 gms U_3O_8/l.

Fe^{+++} concentration - 5.0 gms/l.

SO_4^{--} concentration - 40.6 "

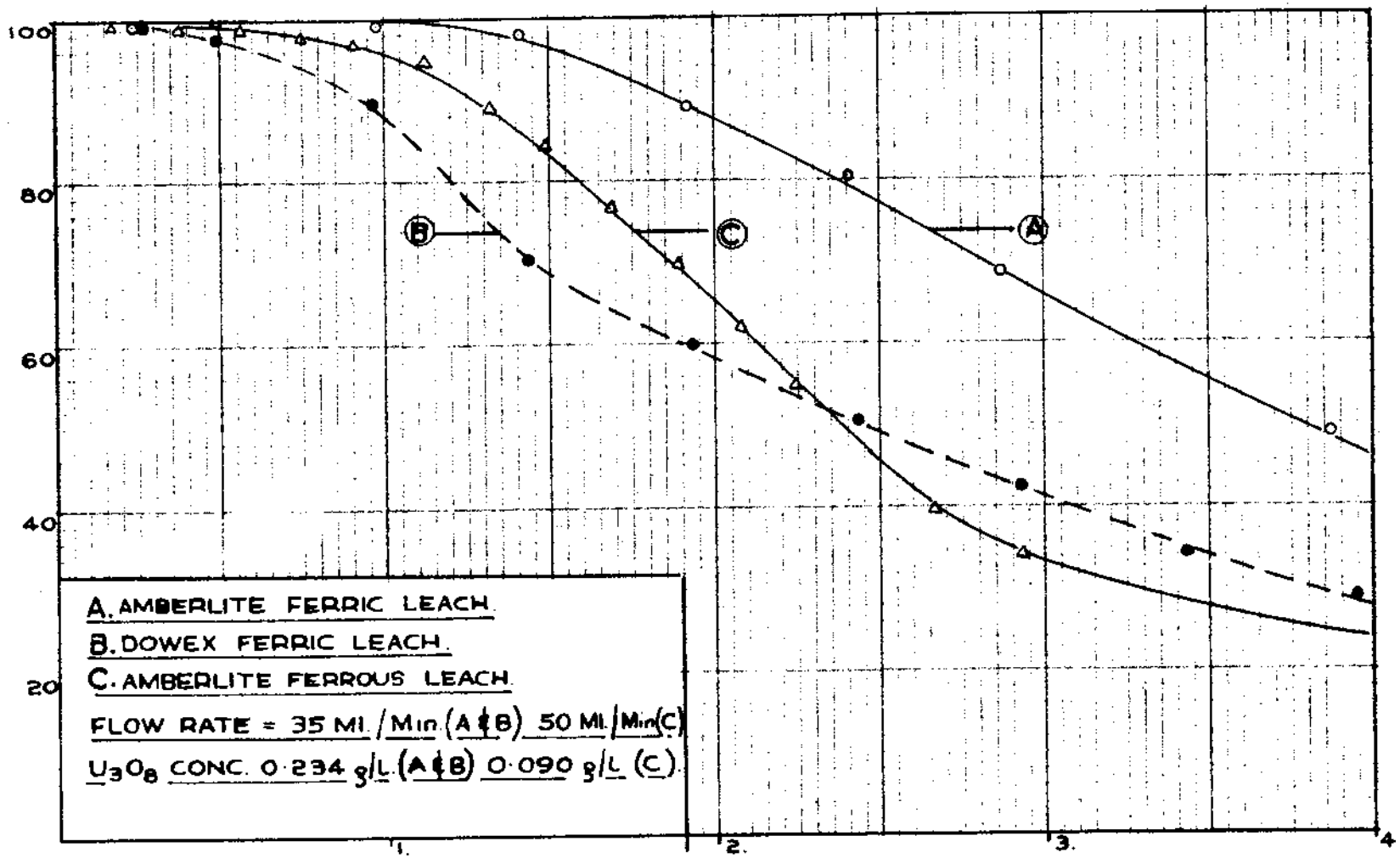
pH - 1.6

The increase in the breakthrough volume and the steeper gradient of the graph after breakthrough shown in these curves, as compared with the previous curves, can be explained as being due to the slower flow rate of 30 mls/minute, which for practical reasons had to be employed.

93/ Loading.....

FIG No 15

LOADING CURVES ON AMBERLITE & DOWEX COLUMNS 400 CYCLES
FERRIC & FERROUS LEACHES



Loading Curves Obtained at 400 Cycles:

At 400 cycles the Blyvooruitzicht Pilot Plant was experimenting with the two stage leaching procedure.[136,138]

In this process the cyanide residue is given a preliminary sulphuric acid leach which removes about 1/3 of the uranium present, together with most of the acid consuming constituents and a portion of the reducing agents present in the ore. The residue from this preliminary leach was then leached with manganese dioxide and sulphuric acid which effects the extraction of the remaining uranium. This procedure results in the saving of manganese dioxide, but produces two solutions, both of which have to be passed through the ion exchange columns. The first solution, known as the ferrous pregnant solution, contains a small amount of uranium and a comparatively large amount of Fe^{++}. The second solution, the ferric pregnant solution, is very similar to that obtained in the normal uranium leach, and contains the major portion of the uranium with Fe^{+++} as the major impurity.

The loading curves of the ferric pregnant solution on the Amberlite and Dowex columns, and the ferrous pregnant solution on the Amberlite column are shown in Figure No 14.

The ferric pregnant solution shows exceptionally good loading characteristics approaching those of a pure uranium solution of the same concentration (Cf Figure No. 12). The ferrous pregnant solution does not exhibit such good loading characteristics, although comparisons are difficult due to the lower concentration of uranium in this solution.

An analysis of the calcined precipitate from the eluate from a column loaded with the ferrous pregnant solution was found to be as follows :-

U_3O_8	-	81.6%
SiO_2	-	19.0%
Fe_2O_3	-	0.43%

94/ These.....

FIG. No. 16.

LOADING CURVES OF AMBERLITE & DOWEX COLUMNS 500 CYCLES

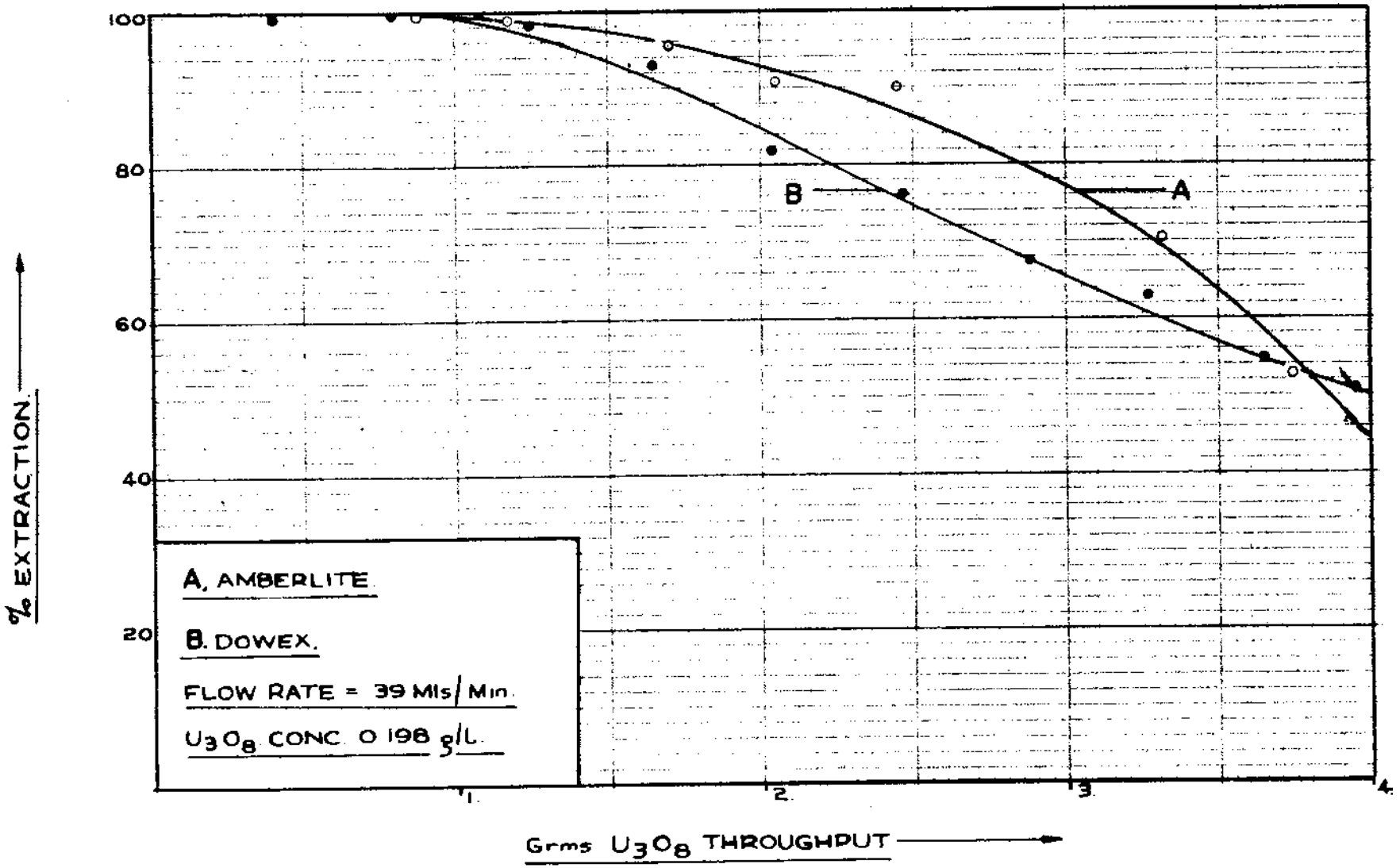
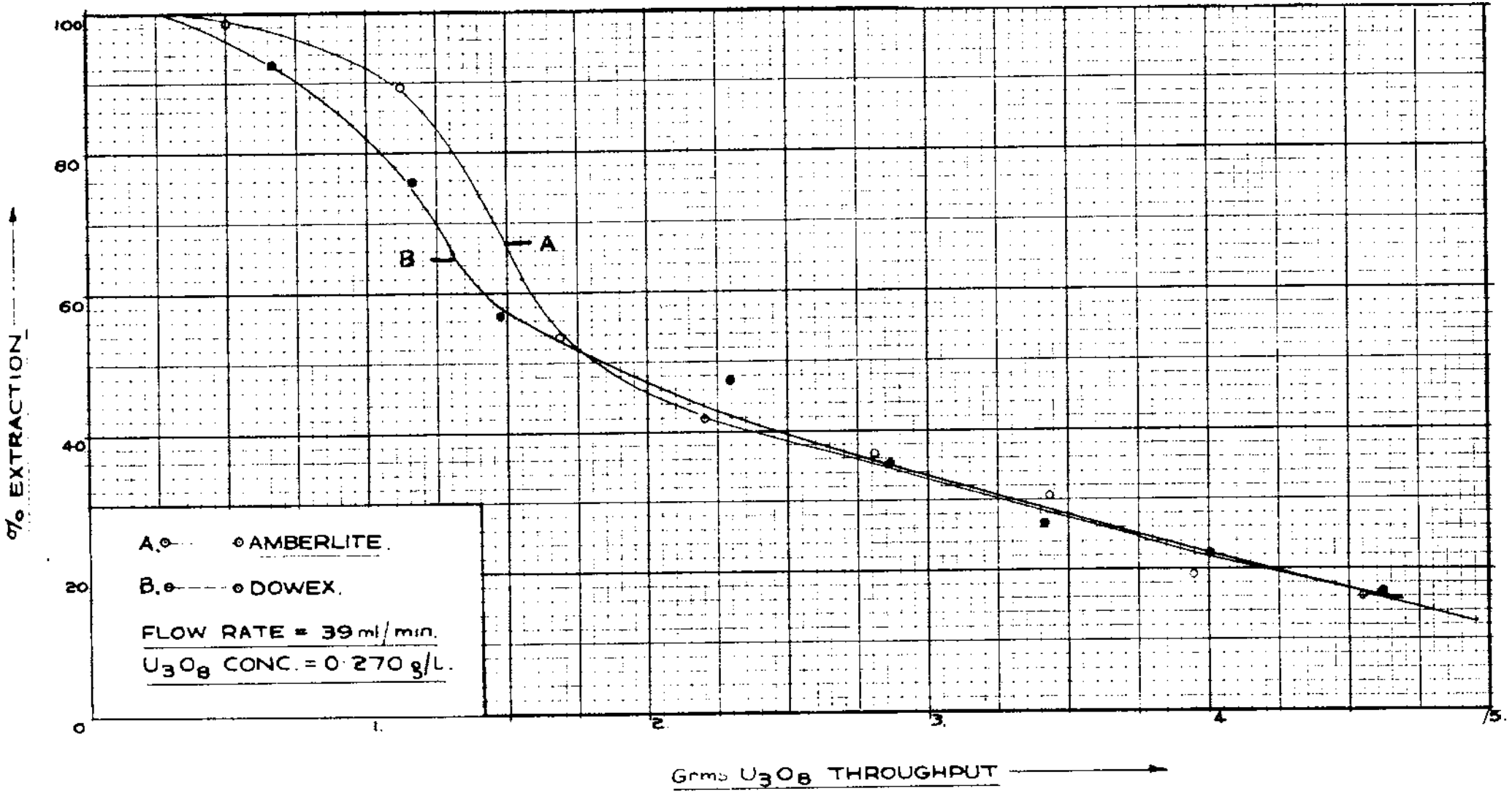


FIG. Nº 17

LOADING CURVES ON AMBERLITE & DOWEX COLUMNS 600 CYCLES.



These results showed that only a very small amount of iron is adsorbed by the resin from such a solution.

Loading Curves Obtained at 500 Cycles.

During this period a mixture of the ferric and ferrous pregnant solutions was obtained from the Blyvooruitzicht Pilot Plant and the loading curves on this solution are shown in Figure No. 16.

Here again remarkably good adsorbtion characteristics were observed but again comparisons were rendered difficult by variations in the composition of this solution compared with those used in previous tests.

Analysis of Solution.

U_3O_8	-	0.198 gms/l.
Fe^{++}	-	0.6 "
Fe^{+++}	-	1.5 "
Sulphate	-	15.81 "
pH	-	2.1

Loading Curves Obtained at 600 Cycles:

Before the 600 cycle Test the Blyvooruitzicht Pilot Plant reverted to the normal single uranium leach. The pregnant solution used for the 600 cycle test was similar in composition to that used at 200 cycles:

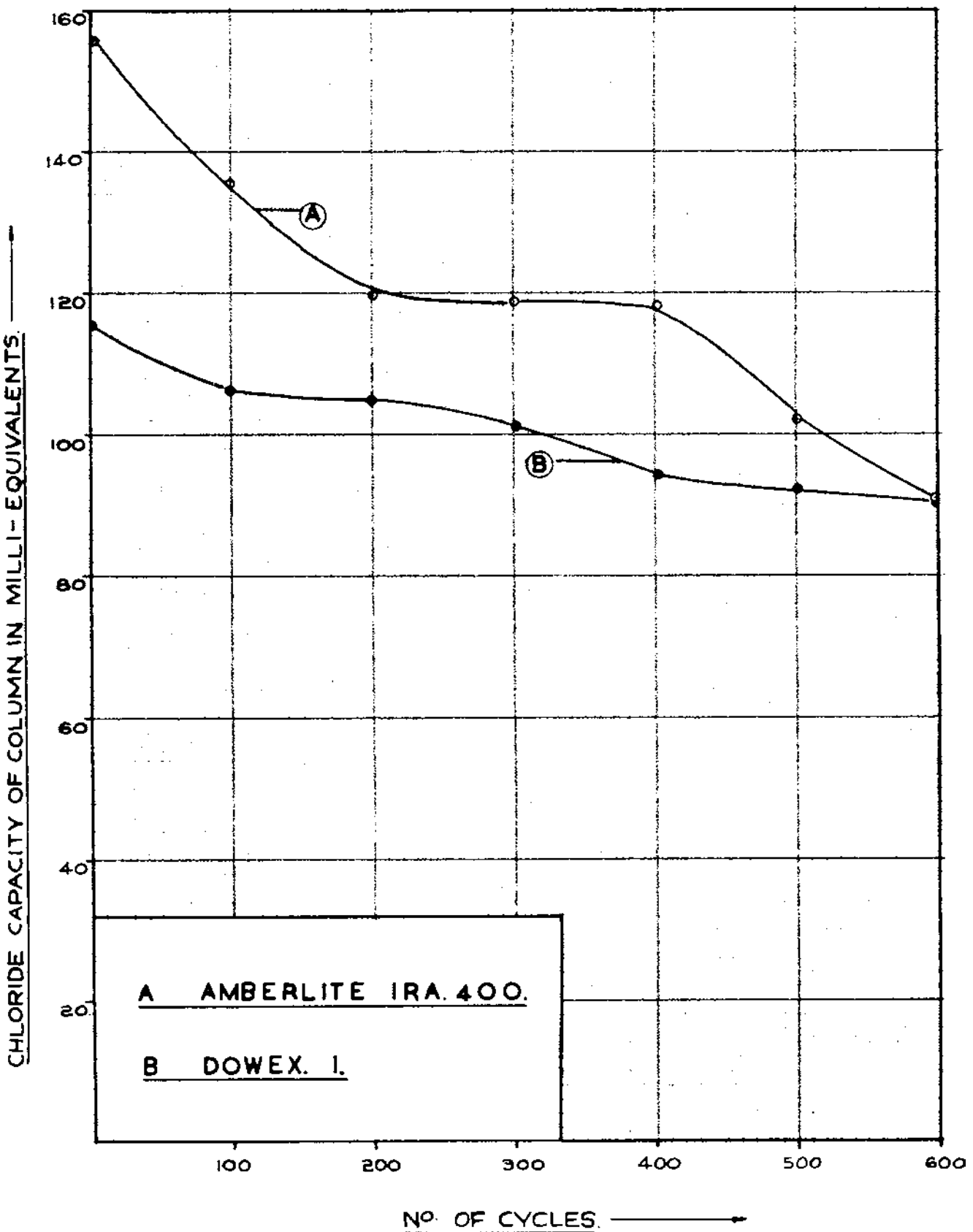
U_3O_8	-	0.270 gms/l.
Fe^{+++}	-	3.85 "
SO_4''	-	33.3 "
pH	-	1.6

The loading curves obtained on this solution are shown in Figure No. 17 which, when compared with the 200 cycle curve, shows a slight improvement in the loading characteristics. This may possibly be due to the slightly higher pH value of the solution.

95/ Chloride....

FIG. No 18

CHLORIDE CAPACITIES OF AMBERLITE & DOWEX COLUMNS O —— 600 CYCLES



Chloride Capacities Measured During the 600 Cycle Test.

In addition to the loading curves described above, the chloride capacities of the two columns were measured every 100 cycles and are given in Table No. 24 and represented graphically in Figure No. 18.

It was observed that the capacity of the Amberlite column drops over the first 200 cycles to approximately 80% of its original capacity and thereafter more slowly to 75% after 400 cycles. From 400 to 600 cycles the drop is more rapid to 57% of its original capacity.

In the case of the Dowex Column there is a slow steady drop over 600 cycles to 78% of its original capacity.

These figures represent the total loss in capacity of the columns, in which is included both chemical poisoning of the resin and also the mechanical loss of the resin from the column.

The actual chloride capacity of the resins expressed in milliequivalents of chloride/gm of resin, which can be taken to represent the amount of poisoning taking place is shown in Table No. 24. These figures illustrate that the resins have not become seriously chemically poisoned during the 600 cycles, their capacities being 88.4% and 92.4% of the fresh resins capacity in the case of the Amberlite and Dowex respectively.

Changes in Weights and Volumes of the Resins over 600 Cycles:

The changes in the weights, volumes and densities of the resins over the 600 cycle period are shown in Table No. 25. During this period the volume of the columns had dropped to 81% (Amberlite) and 90% (Dowex) of the original volume.

The weights of the resins (as calculated from the chloride capacity, since it was desirable to avoid drying of the resin) were only 66.5% and 82.5% of the original weights in the case of Amberlite and Dowex resins respecitvely.

TABLE NO. 24

TABLE NO. 24.

URANIUM AND CHLORIDE CAPACITIES OF [illegible]ERLITE AND DOWEX RESINS DURING 600 CYCLE TEST.

	AMBE[illegible]		DOWEX	
	CAPACITY	% FRESH	CAPACITY	% OF FRESH
1. Chloride Capacity of whole column in milliequivalents of Chloride.				
a) 0 cycles	158		115	100
b) 100 "	136	0	106	92
c) 200 "	120	0	105	91
d) 300 "	119	3	101	87
e) 400 "	118	5	94	82
f) 500	102	5	92	80
g) 600 "	91	4	90	78
2. Chloride Capacity in milli-equivalents Chloride per gm. of Dry RCl				
a) Fresh Resin 0 cycles	3.35		2.53	100
b) 600 cycle Resin	2.86	.4	2.34	92.4
3. Uranium Capacity of whole column in Gms. U_3O_8				
a) 300 cycles	13.6		11.4	
b) 400 "	11.7		7.05	
c) 500 "	8.35		8.05	
d) 600 "				
4. Uranium Capacity in gms U_3O_8/gm Dry RCl				
a) Fresh Resin 0 cycles	0.266	0	.189	100
b) 600 cycles	0.221	3	.146	77.5

TABLE NO. 25

WEIGHTS AND VOLUMES OF THE AMBERLITE AND DOWEX COLUMNS AFTER 600 CYCLES

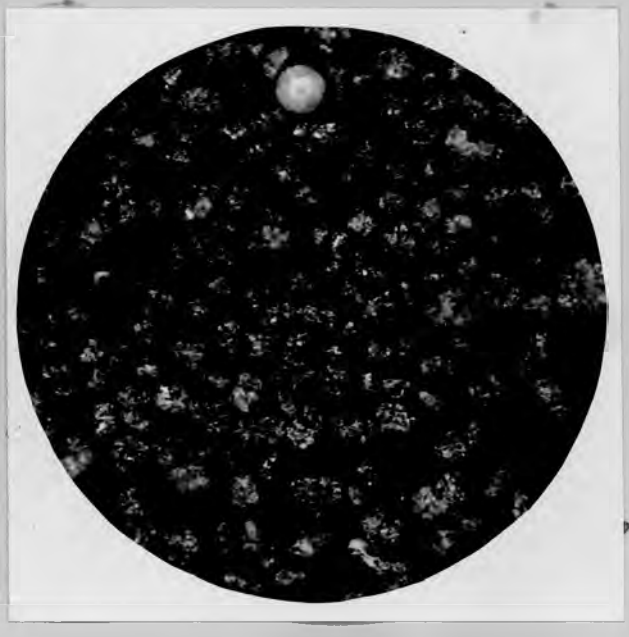
	AMBERLITE		DOWEX	
	VALUE	% OF FRESH RESIN	VALUE	% OF FRESH RESIN
1. Original Column Volume	150 ccs	100	150 ccs	100
Volume after 600 cycles	122 "	81	135 "	90
2. Original Wt. of Resin	46.5gms	100	45.4gms	100
Weight after 600 cycles	30.8 "	66.2	38.4 "	82.5
3. Actual Density in gms dry RCl/cc				
a) Fresh Resin	1.19	-	1.12	-
b) Used Resin 600 cycles	1.25	-	1.17	-
4. Column Density in gms resin per cc. column space				
a) Fresh Resin	0.310	-	0.302	-
b) Resin after 600 cycles	0.254	-	0.284	-

Weights calculated from chloride capacity data

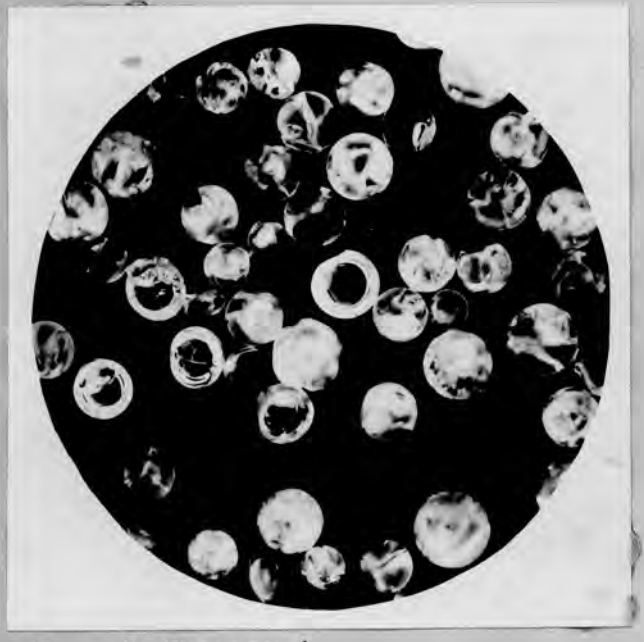
FIG. No. 19.

PHOTOMICROGRAPHS SHOWING DISINTEGRATION OF RESIN DURING THE 600 CYCLE LIFE-TEST

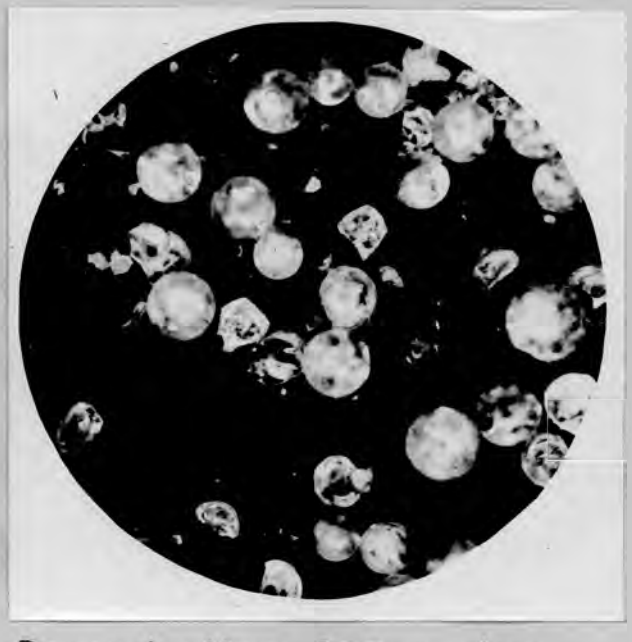
Fresh Amberlite IRA.400



Amberlite IRA 400. After 600 cycles



Fresh Dowex 1



Dowex 1 after 600 cycles

The column densities in gms resin/cc. column space had changed from 0.310 to 0.254 (Amberlite) and from 0.302 to 0.284 (Dowex).

These figures showed that although 33.5% by weight of the Amberlite and 17.5% by weight of the Dowex had been lost during the 600 cycles, the decrease in the volume was not proportional to the amount of resin lost.

Appearance of the Resin:

Figure No. 19 shows four photomicrographs of the fresh and 600 cycle resins. These photographs were all taken at the same magnification and with special precautions to ensure that the samples photographed are representative of the whole mass of the resin.

They show that, particularly in the case of the Amberlite resin, a considerable amount of disintegration had taken place. It appears that during the 600 cycles the large irregularly shaped particles of this resin have disintegrated, the sharp angular corners of the particles having been broken off. This results in more spherically shaped particles and in a narrower range of particle size. In the case of the Dowex resin, the disintegration has taken the form of a fracturing of the originally spherical particles. Some of the fragments of these spheres can be seen in the photograph. However, the disintegration is very much less than in the case of the Amberlite resin.

General Observations on the Operation of the Life Tester During the 600 Cycles.

The main source of trouble encountered in the operation of the life tester during the 600 cycle period was the accumulation of insoluble material in the column. It was observed that a fine, almost colloidal, precipitate separated from the pregnant solution during storage. This precipitate passed

97/ through....

through a sand clarifier and settled from the solution only after long periods of standing. On the passage of the solution through the resin columns a large proportion of this insoluble material coagulated and separated as an insoluble slime on the resin. This occurred on the passage of even an apparently clear pregnant solution through the column.

A qualitative analysis of the slime in the column showed it to consist mainly of silica but also on occasions to contain a fairly large proportion of sulphur.

The presence of this insoluble material necessitated the use of frequent and thorough backwashing of the column. The accumulation of the slime was particularly pronounced during the first 185 cycles of operation. It was noticeably absent when the ferric pregnant solution from the double leaching procedure was employed for the adsorbtion cycles.

On frequent occasions a solid plug, consisting of the finer resin particles cemented together by the slime, formed on the top of the Amberlite resin bed. This in many cases completely stopped the flow of solution through the column. This occurrence became a regular feature during the last 100 cycles of the 600 cycle test.

4. DISCUSSION OF RESULTS AND CONCLUSIONS REGARDING THE FIRST 600 CYCLE LIFE TEST OF THE RESINS.

Conclusions regarding the performance of the resin from the loading curve data were rendered extremely difficult by the varying composition of the pregnant solutions received from the Klyvooruitzicht Pilot Plant. It was considered that the only safe conclusion that could be drawn was that the adsorbtion properties of the Dowex resin, although initially much inferior to those of the Amberlite, gradually improved in comparison to the Amberlite until after 600 cycles the adsorbtion characteristics of the two resins were very similar.

98/ The.....

The most significant result obtained was the rather high disintegration loss of the resin which, in the case of the Amberlite, was found to be much greater than had been anticipated in the preliminary experiments, and exceeded the generally accepted loss of 10% over 1000 cycles. However, it was admitted that the operational conditions employed in this Life Test were more severe than those encountered in most other ion exchange applications.

It was considered that the actual mechanical loss of the resin could be considerably reduced by taking certain precautions. It was obvious that a certain resin loss occurred due to the coagulation of slime around the individual resin particles which resulted in them being carried over with the slime during backwashing. This loss might be considerably reduced by recovering these particles in the backwash effluent and returning them to the column.

At the same time it seemed likely that an inevitable loss due to disintegration of the resin would also occur. It was observed that the decrease in volume of the column was less than the proportional amount of resin lost, or in other words, the apparent column density had decreased. There was virtually no change in the actual density of the resin particles themselves and the only logical explanation for this observation was that the very small particles which had previously filled in the spaces formed between the larger particles had been removed during the backwashing operation. As can be seen when comparing the two photographs of the fresh and 600 cycle Amberlite resins, there is a much narrower range of particle size in the used resin, which would mean a smaller column density. Thus any disintegration of the resin which resulted in the formation of exceedingly small resin fragments must be considered to involve an inevitable loss of resin.

99/ It.....

It is impossible from the results obtained to decide what proportion of the total loss observed represents an inevitable loss and what proportion can be recovered and returned to the column. This matter is of some importance since the choice of the resin to be used in the full scale plants will depend to a certain extent on the mechanical strength of the resin and the amount of unavoidable resin loss that is likely to occur.

It is significant to note that the losses occurring on the Dowex column were much less than in the case of the Amberlite column. Thus, although the Dowex resin has initially only 2/3 of the capacity of an equal volume of the Amberlite resin, the capacities of the two columns after 600 cycles operation are equal. Thus if the unavoidable resin losses are high, it is possible that it would be more economic to employ the resin with the low capacity but higher mechanical strength.

It was for this reason considered advisable to carry out a further Life Test so that the nature of the resin losses could be studied in more detail.

Although the results obtained indicated that the resins after 600 cycles had not suffered any severe chemical poisoning, this possibility could not be excluded in the operation of the full scale plants. In fact the results obtained during the first 100 cycles suggested that exceptional poisoning was indeed taking place but due to certain changes, the significance of which was not understood, this poisoning was not continued.

It was considered, therefore, that the second Life Test should be run on a pregnant solution produced as required under standard conditions resembling those to be used on the full scale plants so that conclusive data regarding the chemical poisoning of the resin could be obtained.

PART II

SECOND LIFE TEST ON AMBERLITE IRA.400, DOWEX I, PERMUTIT SE AND IONAC SE ION EXCHANGE RESINS

1. INTRODUCTION:

In view of the results obtained in the previous life test, it was decided to carry out a repeat test with the object of obtaining more representative data as regards the poisoning of the resin and to determine what fraction of the total loss of resin observed in the previous test represented an unavoidable loss.

It was arranged that the pregnant solution used for these tests was to be produced, as required, at the Government Metallurgical Laboratory from Blyvooruitzicht Cyanide residue under standard leaching conditions resembling those to be used on the full scale plant.

In addition it was decided to include two new resins which had since been received at the Government Metallurgical Laboratory, namely, Permutit SE and Ionac SE resins.

2. LEACHING PROCEDURE AND LIFE TESTER OPERATION.

During the first 300 cycles of operation the cyanide residue received from Blyvooruitzicht was made into a 40% solids slurry and passed over a magnetic separator to remove the metallic iron. After filtration the residue was charged into the pachuca and leached with the desired quantity of sulphuric acid and MnO_2. The MnO_2 used was crushed Pyrolusite, containing 70% available MnO_2, the addition being made one hour after the addition of the acid.

After 16 hours leaching time the pulp was filtered, repulped with water and filtered again, the primary and secondary filtrate being combined to provide the pregnant

101/ solution...

solution for the Life Tester. This solution was passed through a sand clarifier and then pumped into the Life Tester pregnant solution storage drum. Sufficient solution was obtained in one leach to permit operation of the Life Tester for approximately four to five days.

A typical example of the acid and the MnO_2 additions and the analysis of the solutions produced are as follows:

H_2SO_4 added	=	30 lbs/ton
MnO_2 added	=	6 "
Glue ($\frac{1}{2}$ hr. prior to filtration.)	=	$\frac{3}{4}$ "

Analysis of Pregnant Solution:

Fe^{+++}	=	2.0 gms/l.
Fe^{++}	=	trace
Free H_2SO_4	=	2.0 gms/l.
U_3O_8	=	0.25 "
Total sulphate	=	20 "
pH	=	1.8

During the period 300 - 400 cycles the magnetic separation step was eliminated, the cyanide residue being charged directly into the pachuca for leaching. It was found necessary to increase the acid and MnO_2 additions to 50 lbs/ton and 10 lbs/ton respectively.

The operation of the Life Tester was similar to that described in the previous Life Tests. One important difference was that small glass wool filters as shown in Figure No. 26 were included in the glass columns immediately below the backwash water outlet. By suitably packing these filters with glass wool it was found possible to permit the passage of the fine insoluble material but prevent the removal of the larger resin particles during backwashing.

As previously, the accumulation of insoluble material

102/ was.....

was a major source of trouble, particularly in the Amberlite column toward the end of the 400 cycles. One interesting observation in this connection was that the accumulation of insoluble material was particularly severe when no glue additions were made before filtration.

3. EXPERIMENTAL RESULTS:

Changes in Weights and Volumes of the Resins.

Table No. 26 shows the weights and volumes of the resins measured initially and after 400 cycles operation. These figures show that there have been no significant changes in the weights and volumes of the resins originally present, and that the installation of the filters to prevent resin losses during backwashing has been effective in eliminating this source of loss.

Nevertheless this does not imply that no resin disintegration had taken place. In the Amberlite column particularly and to a lesser extent in the Ionac column, the percentage of fine particles had increased, and these fine particles would undoubtedly have been backwashed from the column had the special filters not been included. The resin disintegration will be discussed in more detail later.

TABLE NO. 26

CHANGES IN WEIGHTS AND VOLUMES OF THE RESINS DURING 400 CYCLES

	IONAC	AMBERLITE	DOWEX	PERMUTIT
Initial wt. of resin in gms dry RNO_3	38.5	40.0	46.8	42.6
Final wt. of resin after 400 cycles in gms dry RNO_3	38.0	38.5	46.0	41.3
% Loss in weight	1.3	3.8	1.7	3.0
Initial volume in mls wet settled RNO_3	105	116	100	99
Final vol. after 400 cycles in mls. wet settled RNO_3	115	116	100	99

103/ Chloride....

Chloride Capacities:

Table No. 27 shows the column chloride capacities measured at various intervals during the 400 cycles. It can be seen that minor variations in the total chloride capacity have occurred during the 400 cycle tests. There is, however, no definite cumulative decrease in capacity as was encountered during the previous 600 cycle test where a steady resin loss was occurring. The variations in the capacity can be readily accounted for by the presence of varying amounts of polythionates on the resin as will be discussed later.

TABLE NO. 27

CHLORIDE CAPACITIES OF THE COLUMNS DURING 400 CYCLES.

	Amberlite	Ionac	Dowex	Permutit
Initial column capacity in milliequivalents	134	129	114	119
Capacity after 7 cycles	131	123	102	119
" " 50 "	134	116	108	108
" " 87 "	130	117	100	117
" " 158 "	119	121	100	106
" " 216 "	127	118	106	110
" " 276 "	128	113	105	109
" " 300 "	130	116	115	113
" " 337 "	125	113	106	105
" " 354 "	129	118	113	111
" " 400 "	119	112	102	96

Capacity and Regeneration Tests and Analyses of the Resin

After the completion of 400 cycles, samples of each of the four resins were removed from the columns and subjected to uranium and chloride capacity tests as described in Section C. Analyses for tetrathionate and total sulphur, cobalt and silica were also carried out on these resins.

104/ TABLE NO. 28

TABLE NO. 28

ANALYSIS OF RESINS FOR TETRATHIONATE TOTAL SULPHUR, SILICA AND COBALT

	IONAC	AMBERLITE	DOWEX	PERMUTIT
% S present as tetrathionate	3.41	2.95	3.55	3.60
% Total S present	3.60	3.99	3.60	3.80
% Co on resin	0.061	0.076	0.015	0.014
% Silica on resin	8.0	0.4	trace	3.2

NOTE: The analysis for Co and silica was carried out after the completion of all other tests, since it involves the destruction of the resin.

TABLE NO. 29

URANIUM AND CHLORIDE CAPACITIES OF THE RESINS.

	Uranium cap. % of Fresh Resin	Chloride cap. % of Fresh Resin
Ionac after 400 cycles	64	65
Amberlite after 400 cycles	70	77
Dowex after 400 cycles	81	82
Permutit after 400 cycles	81	79
Ionac after 10% NaOH elution	86	92
Amberlite after 10% NaOH elution	78	89
Dowex after 10% NaOH elution	86	98
Permutit after 10% NaOH elution	83	100

From the analyses of the resins the extent of poisoning due to the polythionate present can be calculated (as shown on Page 49) with the following results:-

	Ionac	Amberlite	Dowex	Permutit
% Poisoning due to Tetrathionate	14.6	12.9	21.5	20.5
Calculated capacity	85%	87%	79%	80%

105/ From.....

From the above figures it can be seen that (a) In the case of the Dowex and Permutit resins the drop in the capacities is fully accounted for by the polythionate present on the resins; (b) In the case of the Amberlite the uranium capacity is lower than the chloride capacity. This has been found to indicate the presence of colloidal sulphur which is confirmed by the difference in the total sulphur and the tetrathionic sulphur present on the resin. This also explains the capacity being lower than that calculated from the analysis for tetrathionate. It will be noted that the 10% NaOH elution, although increasing the chloride capacity of this resin, does not increase the uranium capacity to the same extent. (c) The capacity of the Ionac resin is lower than can be expected from the analysis. There is little evidence of the presence of colloidal sulphur. A similar anomaly was encountered with the Ionac resin from the West Rand Consolidated Plant (Cf page 54) where the measured capacity was found to be lower than the calculated capacity. In both these instances the Ionac resin was observed to contain an abnormally high amount of silica, and it is possible that the presence of this compound is responsible for the anomolous results.

Regeneration Tests.

It was decided to determine whether satisfactory removal of tetrathionates could be obtained by prolonged elution of the resins with the standard 0.1N HNO_3, 0.9N NH_4NO_3 eluting solution. It had previously been observed that the polythionates were removed from the resin by the nitrate eluting solution but at a much slower rate than the uranium, and it was hoped that prolonged elution would provide a very convenient method of regenerating the resin. The resins remaining in the Life Tester were eluted at 5 mls/minute with 5.0 litres of the standard eluting solution. Samples of the resin

106/ were.....

were then removed and their capacities determined. The effluent from the elution was collected and analysed for tetrathionate.

TABLE NO. 30

CAPACITIES OF THE RESINS AFTER PROLONGED NITRATE ELUTION

	% S removed from resin	Uranium capacity % of fresh resin	Chloride capacity % of fresh resin.
Ionac	0.94	69.5	73
Amberlite	0.74	82	90
Dowex	0.48	94	90
Permutit	0.81	83	84

Although an increase in capacity was observed, this method was not considered to provide adequate regeneration of the Amberlite, Ionac and Permutit resins.

In view of the presence of insoluble forms of sulphur on some of the resins a sodium sulphide regeneration was attempted. Further samples of the resins were eluted with a 5% sodium sulphide solution, followed by dilute nitric acid wash. The capacities of the resins were determined.

TABLE NO. 31

CAPACITIES OF THE RESINS AFTER SODIUM SULPHIDE REGENERATION

	Uranium capacity % of fresh resin	Chloride capacity % of fresh resin
Ionac	79	74
Amberlite	94	91
Dowex	95	92
Permutit	97	(88)

Except in the case of the Ionac resin satisfactory regenerations were obtained. However it was noticed that in this treatment much sulphur was precipitated and on allowing

FIG Nº 20.

LOADING CURVES. AMBERLITE IRA 400.

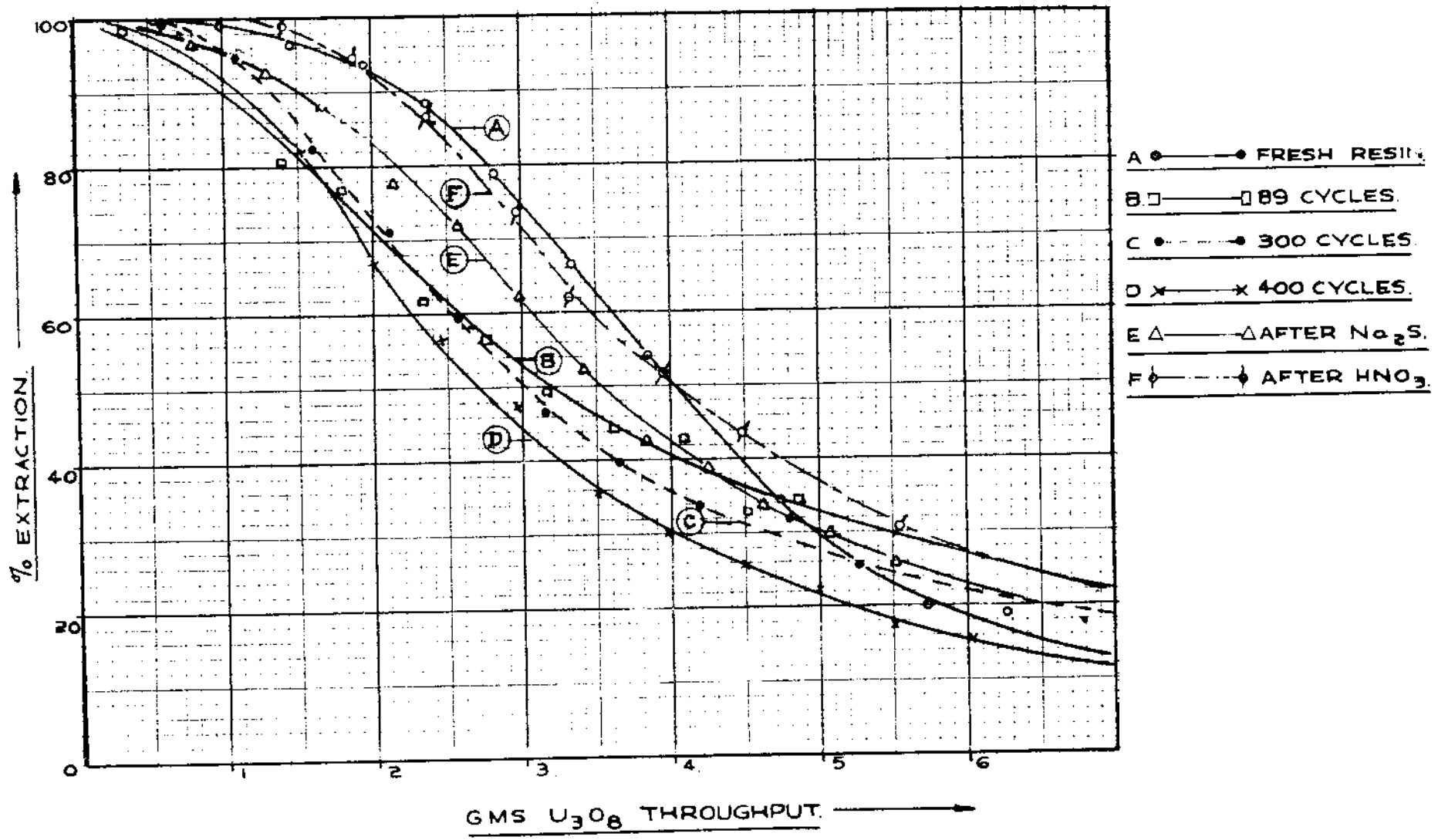


FIG. Nº 21.

LOADING CURVES IONAC. RESIN.

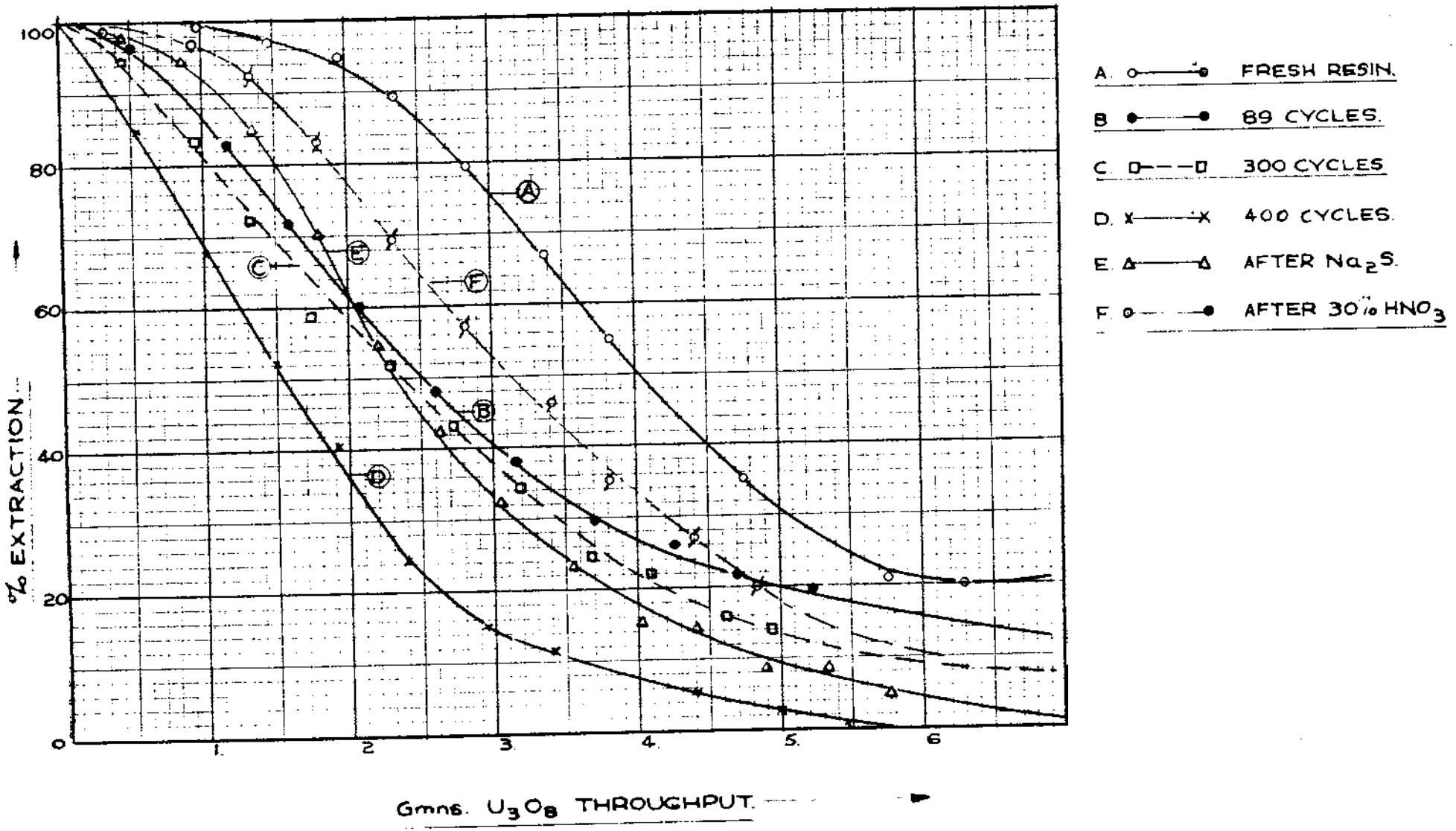


FIG Nº 22.

LOADING CURVES. DOWEX 1.

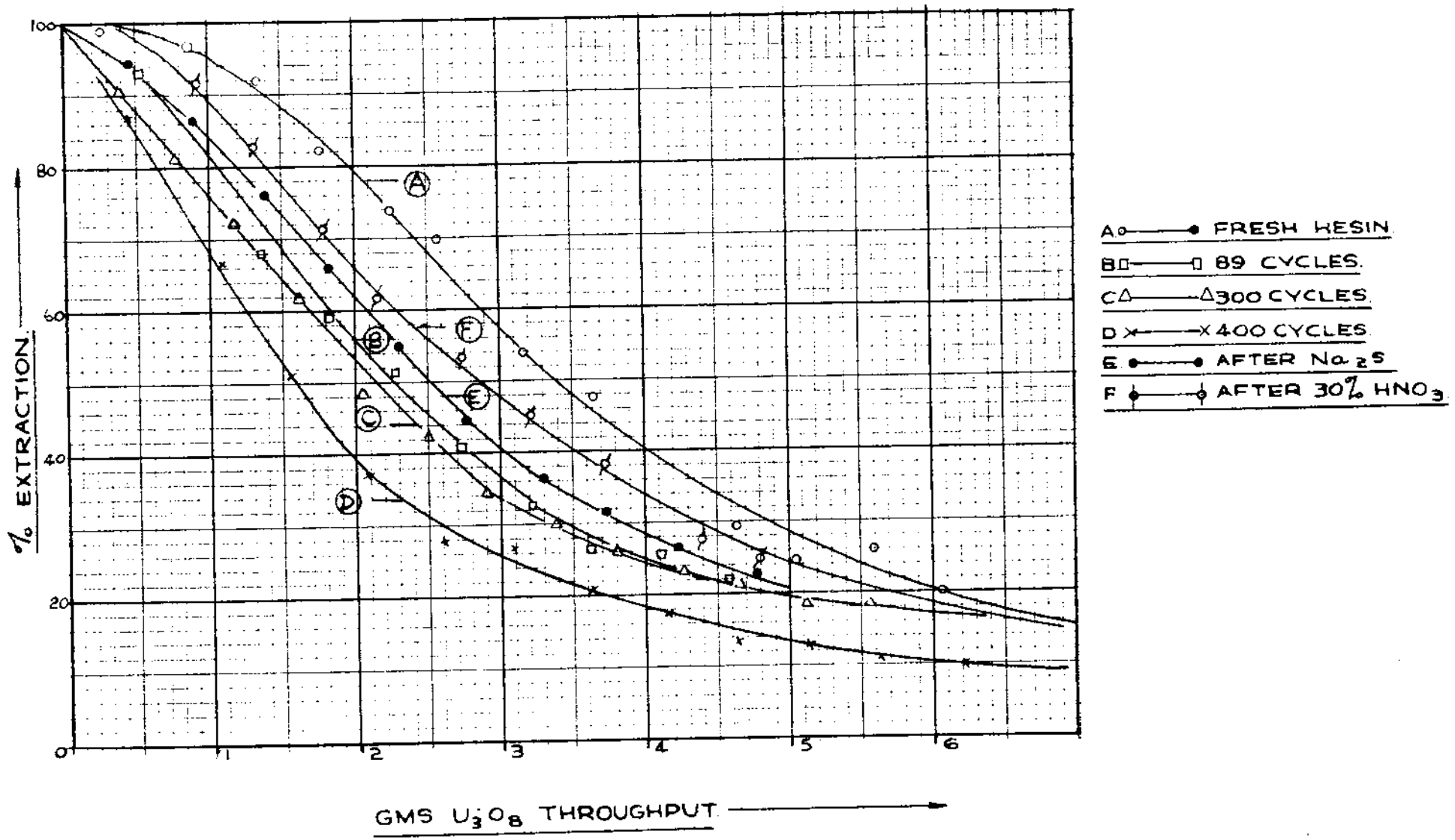
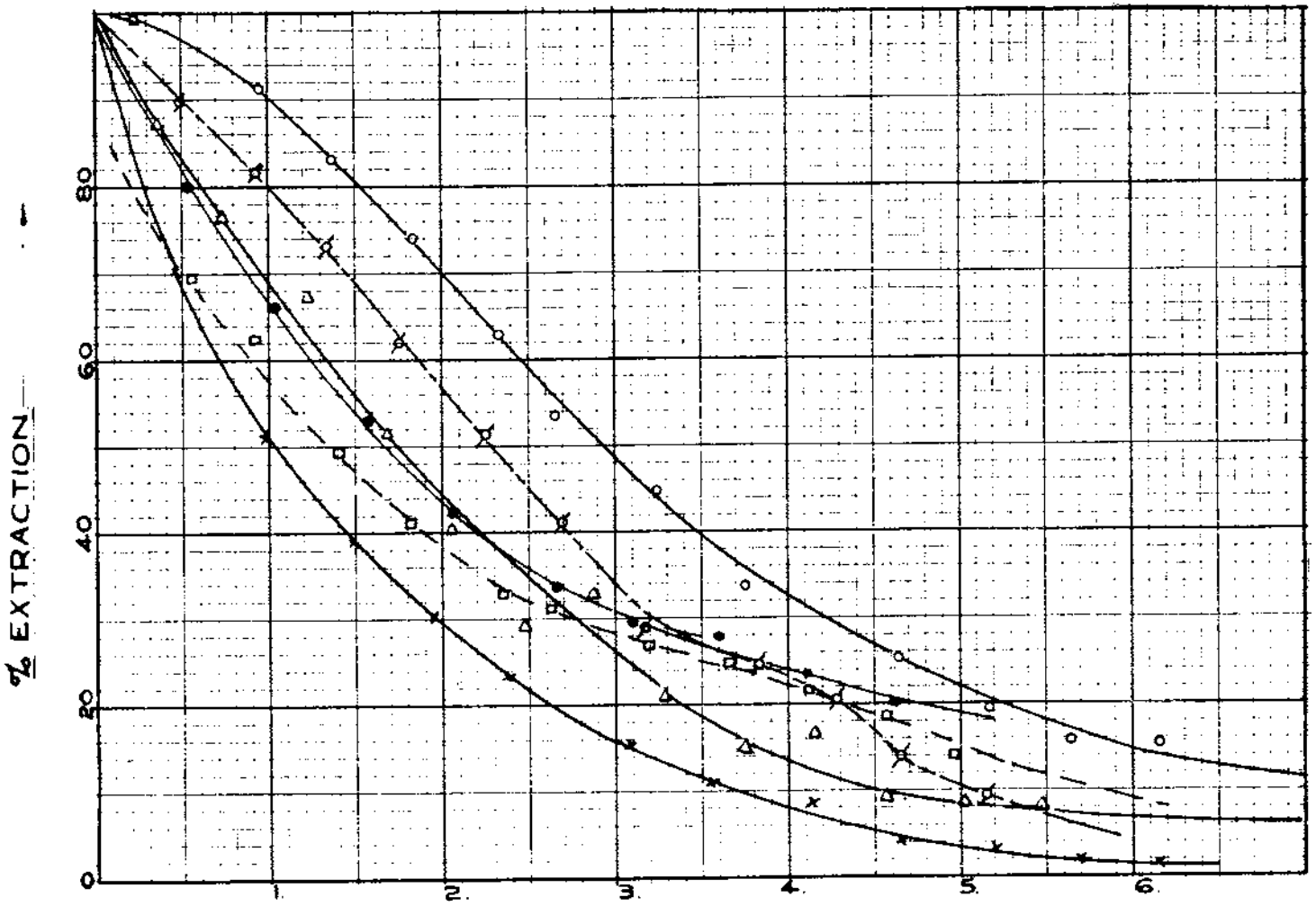


FIG. Nº 23.

LOADING CURVES. PERMUTIT SE.



the resins to stand in 30% nitric acid after the sulphide regeneration for two days, even higher capacities were obtained.

TABLE NO. 32

CAPACITIES OF THE RESINS AFTER SODIUM SULPHIDE REGENERATION FOLLOWED BY 30% NITRIC ACID.

	Uranium capacity % of fresh resin	Chloride capacity % of fresh resin.
Ionac	79	81
Amberlite	97	96
Dowex	97	98
Permutit	98	96

The remainder of the resins in the Life Tester were then given a 5% sodium sulphide regeneration followed by allowing them to stand in 30% nitric acid for three days. Loading curves obtained after these treatments confirmed that satisfactory regenerations had been achieved.

Loading Curves on Pregnant Solutions.

During the 400 cycles loading curve tests were carried out on the fresh resin at 89, 300 and 400 cycles, after sodium sulphide regeneration, and after 30% nitric acid treatment. The curves obtained from these tests are shown in Figures Nos. 20 to 23.

In these curves the percentage of uranium extracted at any particular instant by the column is plotted against the total amount of uranium that has passed through the column. These two variables were calculated as follows:

$$\% \text{ extraction} = 100\left(1 - \frac{\text{Concentration of } U_3O_8 \text{ in effluent}}{\text{Concentration of } U_3O_8 \text{ In influent}}\right)$$

Gms. U_3O_8 Throughput = Vol. throughput x conc. of U_3O_8 in influent

In this way it was hoped to allow for small variations

108/ in.....

in the composition of the pregnant solutions, so that comparable curves could be obtained. It was appreciated, however, that only an approximate comparison could be made since other factors such as the Fe^{+++} conc, the pH and the SO_4" conc. in the pregnant solutions had a marked effect on the shape of the loading curve. In addition, due to variations in the different batches of cyanide residue received, it was impossible to produce pregnant solutions of constant composition for these loading curve tests.

Nevertheless it was considered that the following facts were evident from a consideration of the loading curves shown in Figures Nos. 20 to 23.

(a) The initial loading curves in all cases indicate superior adsorbtion characteristics to those obtained after the resin had been in use for a number of cycles. The phenomena has been observed in many other instances.(See pages 29, 89.) The curves obtained at 89 and 300 cycles are essentially very similar, and can be considered to be typical of the normal operating characteristics of the resins on Blyvooruitzicht pregnant solutions.

(b) In the case of the Amberlite resin, the loading curve obtained after complete regeneration of the resin with sodium sulphide and nitric acid is almost identical with the initial loading curve of the fresh resin. This shows that no irreversible change has occurred in the resin itself (such as a loss of exchange groups or permanent mechanical blocking of the resin) during the 400 cycles. In the case of the Dowex and Permutit resins the loading curves after regeneration do not exhibit adsorbtion properties equal to the fresh resin. This cannot be attributed to a loss of exchange capacity, since the chloride and uranium capacities after regeneration are almost identical with the fresh resin capacity. The decrease

109/ in.....

in the adsorbtion characteristics must therefore indicate a decrease in the rate of reaction brought about by some change, possibly a mechanical blocking of the resin particles. In the case of the Ionac resin, the very marked inferiority of the loading curves after regeneration compared with those of the fresh resin can be attributed to both a decrease in capacity and in the rate of reaction.

(c) The decrease in the adsorbtion characteristics of the Ionac, Dowex and Permutit resins after a few cycles operation is very much more pronounced than in the case of the Amberlite resin.

(d) The loading curves obtained at 400 cycles illustrate a further drop in the adsorbtion characteristics of the resin compared to those obtained at 89 and 300 cycles. It must be remembered that during the period 300 - 400 cycles no magnetic separation step was used prior to leaching. In view of the experience obtained during the investigations on the formation of polythionates in connection with the Western Reefs poisoning, it was apparent that the elimination of this additional washing step would result in a greater amount of tetrathionate in the pregnant solution and consequently a greater degree of poisoning on the resin during the period 300 - 400 cycles.

(4) DISINTEGRATION TESTS

It is obviously impracticable to subject all the various resin samples received to a life test in order to determine their attrition resistant properties. It was desirable, therefore, to devise a more rapid test for determining this property. As a result of the life test described above it was possible to predict with some certainty in what way resin disintegration losses occurred, and thus to devise some simple test to measure these losses.

There appeared to be three sources of resin losses.

(a) Solubility losses, brought about by the very slight solubility of the resin in the various aqueous solutions used on the Rand. These losses cannot automatically be considered to be negligible. The presence of a yellow colour in the recycled barren eluting solution, which was identified to be due to organic material, suggested that the solubility of the resins in acid solutions over a large number of cycles might be appreciable. However, in the life test described, the small resin losses observed can be adequately accounted for by back-washing losses, and it is apparent that virtually no dissolution of the resin had occurred.

(b) Disintegration losses brought about by "acid shock".

This source of disintegration was discussed with Dr. Winters and Dr. Kirk of the Rohm and Haas Co. U.S.A.

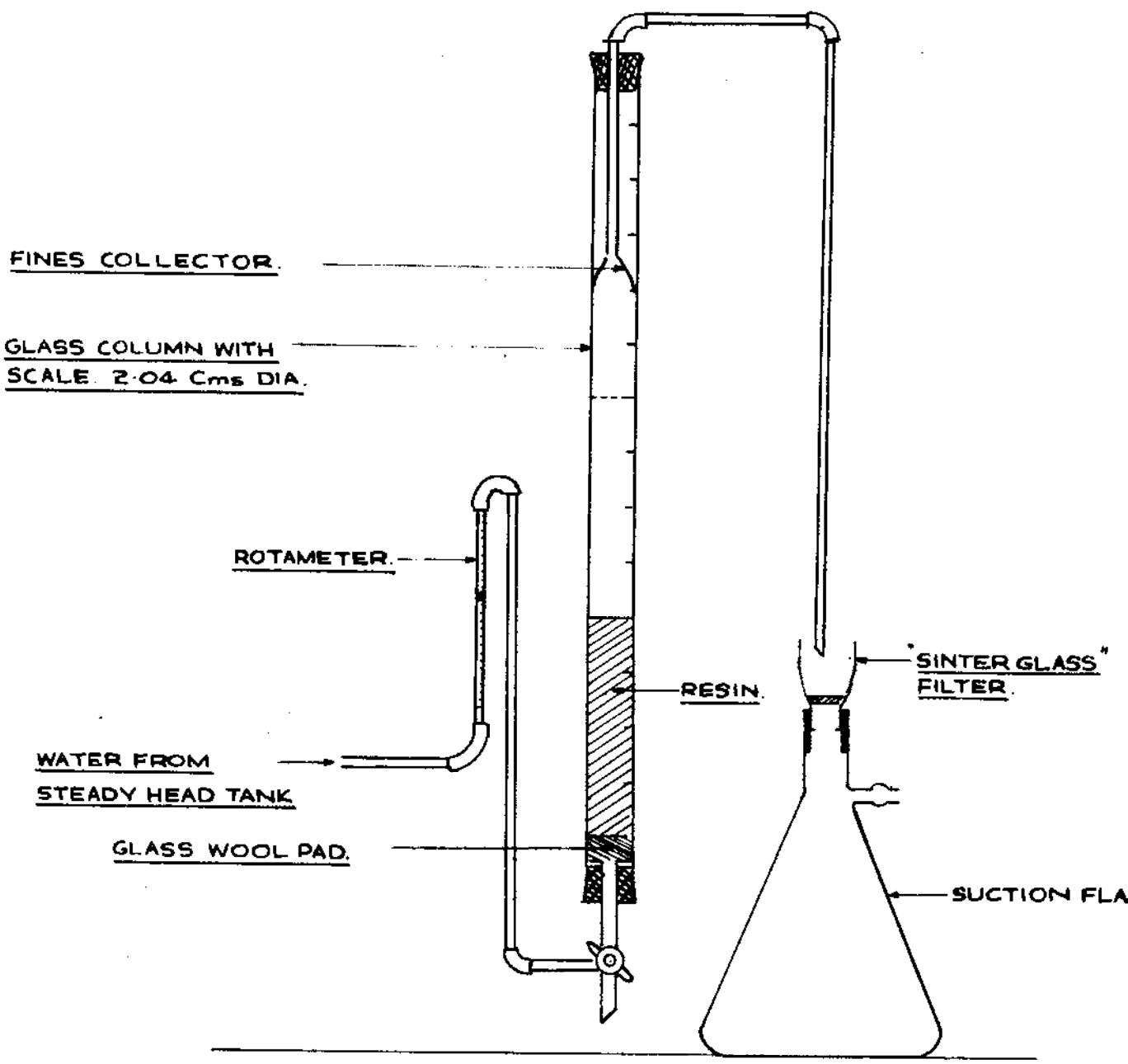
It appears that certain resins are sensitive to sudden changes in ionic concentrations, which bring about their sudden disintegration. This phenomenon is a fairly common occurrence with the phenol-formaldehyde based resins, but only occurs with the polystyrene based resins (which are the type in use on the Rand) if insufficient cross-linking had been employed in their manufacture. A complete understanding of this type of disintegration has not yet been achieved, but there appears to be a critical degree of cross-linking, above which the resins are stable, and below which sudden disintegration occurs suddenly, usually accompanied by marked changes in appearance and densities of the resins. No such effects have been observed in the operation of the resins in the life tester, and it is considered improbable that any such disintegration occurred.

(c) The slow disintegration of the resin into very small particles brought about by the constant pressure and frictional abrasion occurring in column operation. This results in the production of exceedingly fine particles which are readily removed during the back-washing operation. Although some of the coarser resin

111/ particles.....

FIG. Nº 24.

BACKWASHING APPARATUS FOR RESIN FINES DETERMINATION.



particles removed can be screened off from the backwash effluent and returned to the column, this is not advisable with the very small particles since their presence gives rise to a mechanical blocking of the column requiring high solution pressures to maintain normal flow rates. In the operation of the life tester these fine particles were retained in the columns by the glass wool filters and resulted in a great deal of operational difficulties, particularly in the Amberlite column towards the end of the 400 cycle test. It is considered that this is the major source of resin loss likely to occur in the operation of the ion exchange resins.

Any simple test which provides a measurement of the mechanical strength and abrasion resistant properties of the resin can be expected to measure the relative suitabilities of the resins as regards their disintegration losses during column performance. In addition an artificial test which would bring about a slow steady type of disintegration, would be more representative of the actual disintegration occurring in column operation than any other more severe test resulting in a large percentage of fine particles. It was, therefore, of advantage to develop a method whereby a very small increase in the percentage "fines" of the resin could be measured. This was achieved as described in the following disintegration test.

Artificial Disintegration Tests.

50 mls. of the wet settled nitrate form resin were introduced into the backwashing apparatus shown in Figure No. 24. The height of the resin bed was noted and the resin backwashed at a flow rate adjusted to give 100% bed expansion. Backwashing was continued until no more fines were observed to be removed from the resin bed. The resin was then transferred quantitatively into a 250 ml. glass stoppered cylindrical bottle into which were introduced ten $\frac{1}{4}$" diameter glass beads, each weighing

112/ 0.25 gms.....

TABLE NO.33.

Disintegration Tests

RESIN	INITIAL SETTLED VOLUME.	SETTLED HEIGHT.	TOTAL CHLORIDE CAPACITY	WEIGHT OF BEADS	TOTAL AGITATION TIME.	BACKWASH FLOW RATE	EXPANDED VOLUME	% EXPANSION	CHLORIDE CAPACITY OF SLIMES	% DISINTEGRATION LOSS.
Amberlite IRA 400 Received March 1951	50 ml	6.95"	61.0m.eq	2.50	30 Days	46 ml/min	14.5-15.0	100	2.15	3.7
Subjected to Life Test at the G.M.L.	"	6.95"	57.3 "	2.50	60 "	" "	"	100	2.30	7.7
	"	7.00"	53.3 "	2.50	90 "	" "	"	100	2.20	11.8
Amberlite IRA 400 Ex West Reefs Pilot Plant	"	7.00"	60.0 "	2.52	30 "	" "	"	100	0.31	0.5
Amberlite IRA 400 Ex West Rand Cons. Plant	"	6.95"	63.0 "	2.53	30 "	46 "	"	100	0.25	0.4
Permutit SE	"	7.00"	43.6 "	2.49	90 "	66 "	"	100	0.23	0.5
Compound A (Rohm & Haas)	"	6.95"	45.6 "	2.50	90 "	30 "	14-15	100	0.11	0.24
WL. 1602 (Rohm & Haas)	"	6.95"	76.0 "	2.51	90 "	60 "	"	100	0.46	0.60
Ionac	"	7.10"	64.0 "	2.51	90 "	66 "	"	100	<0.10	<0.1
Dowex I	"	7.00"	61.5 "	2.53	90 "	66 "	"	100	<0.10	<0.1

0.25 gms. The total volume of the resin, beads and water was adjusted to 100 ml. The bottle was agitated on rolls at a rate of 60 r.p.m. for a specified time, usually one month.

After this period the resin was returned to the backwashing apparatus and backwashed under exactly the same conditions as before. The fines were collected quantitatively by filtration of the backwash effluent through a sinter glass Gooch crucible. Backwashing was continued until no more particles were observed to be removed, which in many cases took as long as two or three hours.

The total chloride capacities of the resin remaining and of the fines collected were then determined. The latter determination was carried out without removing the fines from the crucible by repeated washings with a 1.0N HCl solution followed by a water wash and then complete removal of the chloride adsorbed with 0.9N NH_4NO_3 and 0.1N HNO_3, this effluent being analysed for chloride.

This procedure enabled the percentage loss of the resin to be calculated on the basis of the chloride capacities.

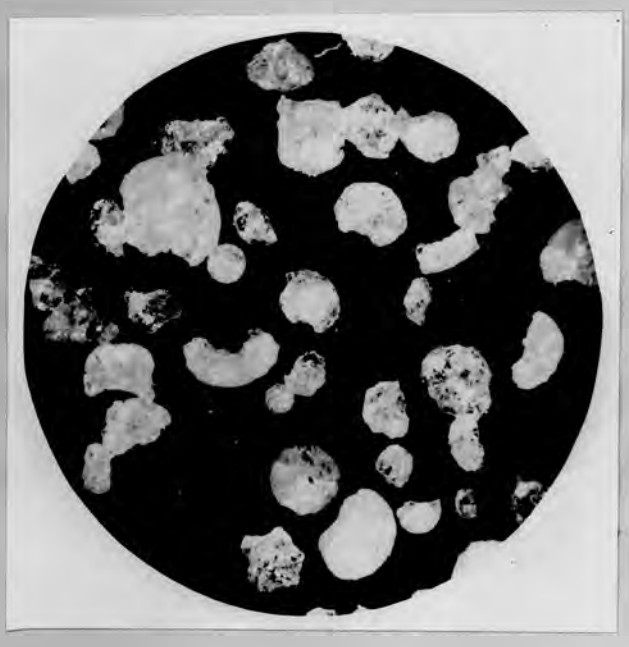
Results:

Table No. 33 shows the results obtained from these tests on the various resin samples received at the Government Metallurgical Laboratory. It is shown that the particular sample of Amberlite IRA.400 resin used in the Life Tester, experienced a far greater disintegration loss than any of the other resins tested. This sample was the first batch of this resin to be received at the Government Metallurgical Laboratory, and, as pointed out by the manufacturers, was produced at a time when the technique of manufacture was still in the experimental stage. Samples of the Amberlite IRA.400 resin received at a later date, namely those supplied to the Western Reefs Pilot Plant and the West Rand Consolidated Plant, experienced only $\frac{1}{6}$ of the disinte-

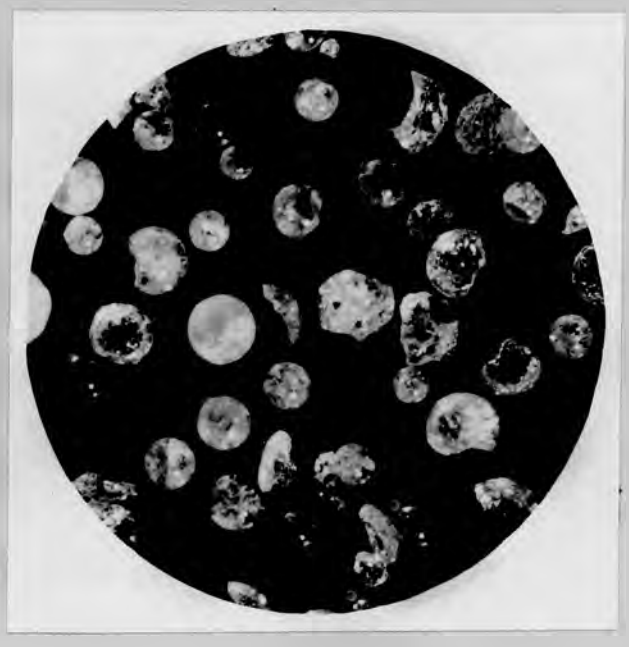
TABLE NO. 33

FIG. No. 25.

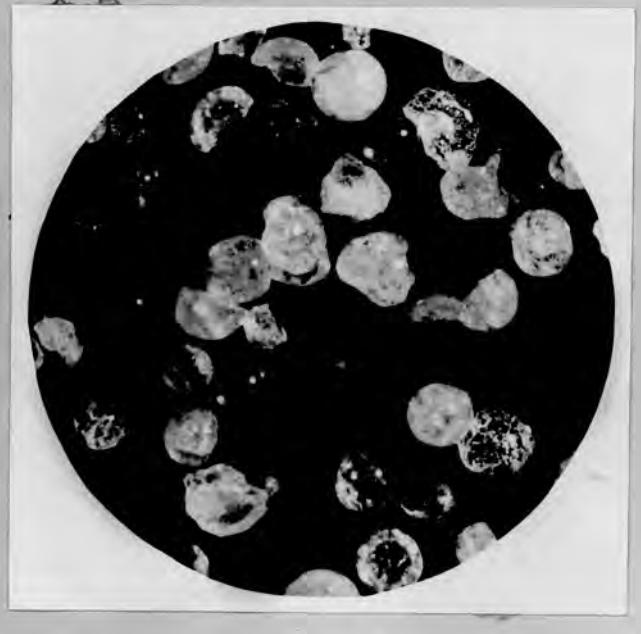
PHOTOMICROGRAPHS OF VARIOUS RESINS.



Amberlite IRA 400. Original sample from Rohm & Haas. Used in life test.



Amberlite IRA 400. Sample supplied to Western Reefs pilot plant.

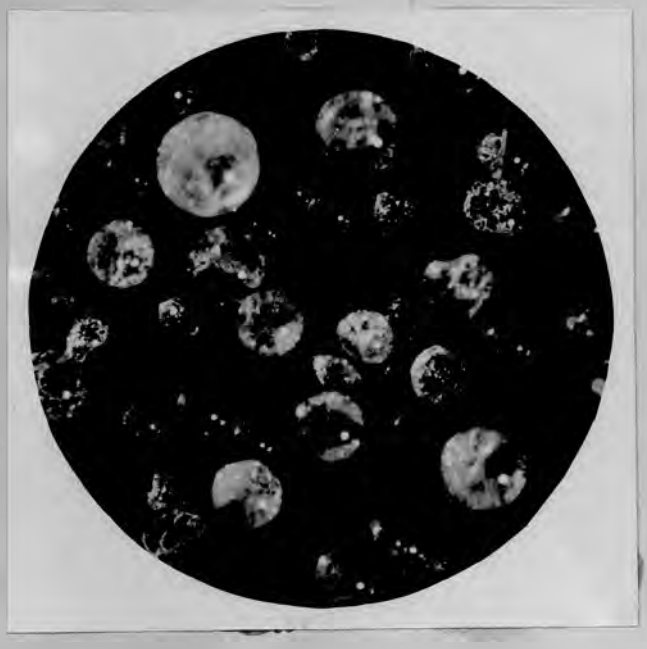


Amberlite IRA 400. Sample supplied to West Rand Consolidated plant.

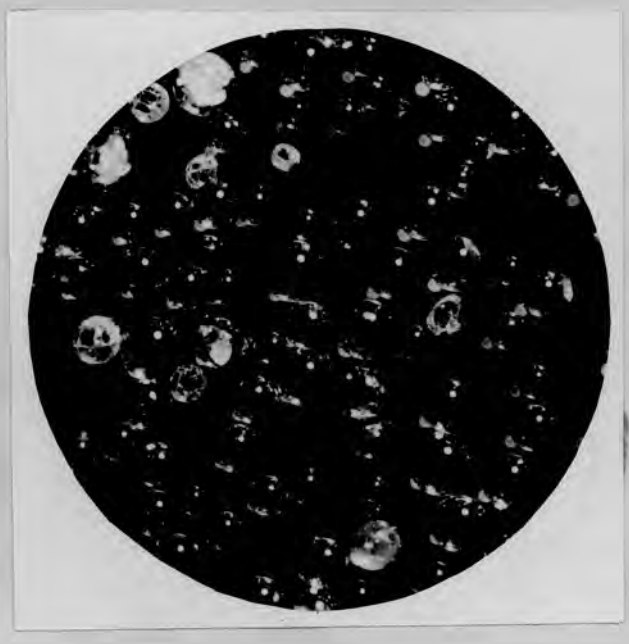
Dowex 1. As used in life test.

FIG No 25

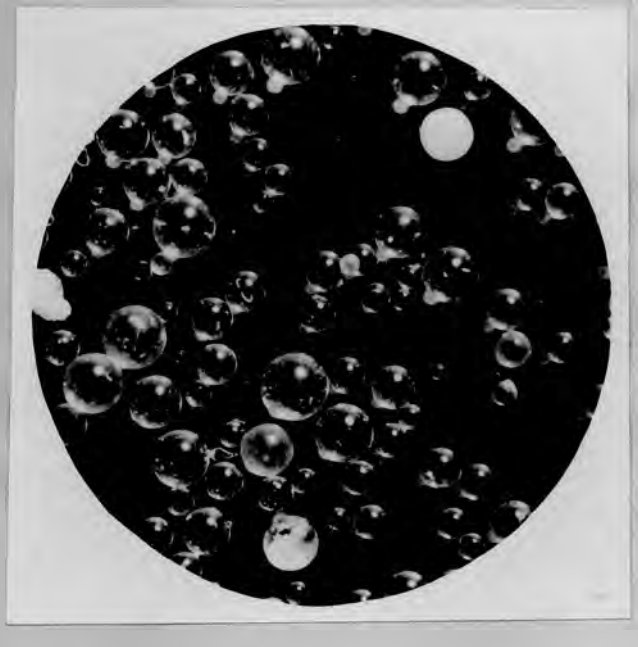
PHOTOMICROGRAPHS OF VARIOUS RESINS



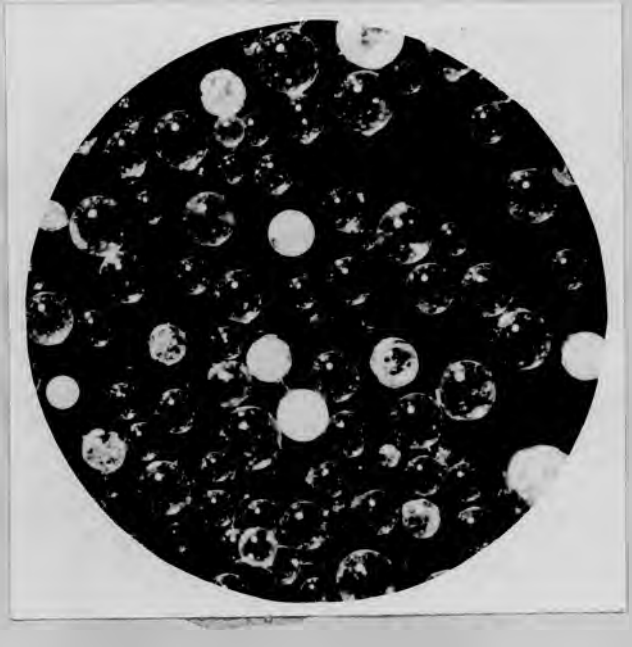
Compound W.L 1602



Ionac. As used in life-test



Compound "A"



Permutit S.E. As used in life-test.

gration loss of this original sample of Amberlite.

A ready explanation for the difference in the disintegration values is provided when photomicrographs (shown in Figure No. 25) are compared. The original sample of Amberlite IRA.400 can be clearly seen to consist entirely of irregularly shaped particles with an extremely fractured appearance. The other two samples of the Amberlite resin, although containing a proportion of such particles, consists mainly of truly spherical particles, which can be expected to be very much more resistant to abrasion and disintegration. The other resins such as Dowex I, Ionac, Compound A and Permutit SE, which have very small disintegration losses, are shown to consist almost entirely of truly spherical particles, only a few of which show signs of fracturing. The resin W.L. 1602 is intermediate in appearance between the Amberlite resins and the truly spherical resins and is found to have a disintegration loss intermediate between these two.

It is significant to note that in the case of the resins manufactured by Rohm and Haas, the order of increasing percentage cross-linking is Compound A < Amberlite IRA.400 < Compound W.L. 1602. The disintegration losses, however, are 0.24%, 3.7% and 0.6% which do not follow the same sequence, and suggest that the percentage cross-linking is but a minor consideration as regards resistance to abrasion, when compared with the shape and nature of the individual particles.

A rough estimate of the expected loss of resin over a given number of cycles can be obtained by a correlation of the data obtained from the above tests with the actual loss experienced during the operation of the life tester. This latter value was obtained by backwashing the Amberlite column in the life tester after 3 cycles, collecting the fines removed

114/ in.....

in the effluent and measuring their chloride capacity.

The chloride capacity of these fines was found to be 6.23 milliequivalents, i.e. 4.6% loss over 300 cycles or, assuming a constant rate of disintegration, a 15% loss over 1,000 cycles. This loss is considerably less than that experienced in the first life test of the Amberlite resin over 600 cycles, but it must be remembered that in this test no filters had been installed to prevent the loss during backwashing of the larger resin particles occluded in the coagulated slime. The figure given in the second life test represents an unavoidable loss and does not include the larger resin particles which are removed during backwashing but can, by suitable screening of the effluent, be returned to the columns.

Thus calculating the expected loss of the other resins, assuming this to be proportional to the disintegration figures shown in Table No. 33, the following figures were obtained:

TABLE NO. 34

EXPECTED DISINTEGRATION LOSSES OF VARIOUS ANION EXCHANGE RESINS

	Loss in disintegration Test. % loss per 90 days.	Calculated expected loss over 1000 cycles %
Amberlite IRA.400 Ex Life Tester	11.8	15.0
Amberlite IRA.400 Ex West. Reefs	1.5	1.9
Amberlite IRA.400 Ex W. Rand Cons.	1.2	1.5
Compound W.L. 1602	0.6	0.76
Permutit SE	0.5	0.64
Compound A	0.24	0.30
Ionac	< 0.1	< 0.1
Dowex I	< 0.1	< 0.1

115/ It.....

It must be emphasised however, that these figures are not intended to represent an accurate estimation of the expected loss of the resin, but merely to obtain some idea as to whether disintegration losses will prove to be a major consideration in the life of the resin.

116/ CONCLUSIONS.....

CONCLUSIONS REGARDING THE LIFE OF THE ION EXCHANGE RESINS OPERATING ON THE BLYVOORUITZICHT PREGNANT SOLUTIONS

The following conclusions can be drawn regarding the life of the anion exchange resins operating on Blyvooruitzicht pregnant solutions, from the results of these life tests.

1. The only serious type of chemical poisoning encountered in the life test of the resins on the Blyvooruitzicht pregnant solutions was the adsorbtion of tetrathionate anions. This had the effect of decreasing the adsorbtion characteristics of the resins after only a few cycles, but only to the extent of approximately 20% of the original capacity. This poison, however, did not accumulate on the resin, since it is partially removed during the nitrate elution and a type of equilibrium is established whereby excessive amounts of tetrathionate are removed in the eluting solution. The overall effect is that the resins operate at only approximately 80% of their fresh capacity.

On standing, the tetrathionates decompose and sulphur is precipitated inside the resin. This has a serious effect on the adsorbtion properties of the resin, and precautions should be taken on the full scale plants to ensure that resin containing the tetrathionate should not be allowed to stand in this condition.

During the first 100 cycles in the first life test exceptionally severe poisoning occurred on the resin. Although at the time the nature of the poisons was unknown, it is now apparent, after the completion of the tests on the Western Reefs resins and the life tests on the Blyvooruitzicht pregnant solution, that this poisoning was due to an excessive amount of polythionate in the Blyvooruitzicht pregnant solution produced at that time. It is difficult to explain the reason for this exceptional concentration of polythionate. Inquiries at the Pilot Plant have failed to reveal any significant changes in

117/ the.....

the leaching or cyanidation procedure. It is possible that the ore treated at that particular time contained an exceptional amount of sulphur compounds which would form tetrathionates during the leach. At no other time during the life test of the resins was such serious poisoning encountered. Nevertheless the possibility of very severe tetrathionate chemical poisoning taking place under exceptional conditions must be anticipated.

However, even in such cases, the tetrathionate anion and precipitated sulphur can be efficiently removed with 5% Na_2S followed by soaking the resin in 30% HNO_3.

2. The amount of cobalticyanide poison adsorbed on the resin was negligible and it is apparent that the Blyvooruitzicht Plant will not experience trouble in this respect. The possibility of the formation of cobalticyanide during the addition of a manganese dioxide slurry containing cobalt, to a pulp containing cyanide prior to the addition of leaching acid must be borne in mind. In the life test described, the MnO_2 was introduced after the addition of all the leaching acid, and it is understood that this is the procedure adopted at the Blyvooruitzicht Plant, in which case the possibility of cobalticyanide formation is eliminated.

3. The resin losses encountered during backwashing can be considerably reduced by the installation of some form of trap to catch the larger resin particles removed, so that they can be returned to the column. An unavoidable loss does occur due to the disintegration of the resin. This disintegration appears to be due to the mechanical abrasion occurring in the column and resulting in the production of exceedingly fine particles of resin, which have to be removed to permit trouble free operation of the columns. Except in the case of the first sample of Amberlite received at the Government Metallurgical Laboratory, this unavoidable loss is negligibly small and does

not warrant consideration as a major criterion in the choice of the most suitable resin to be used for Uranium extraction at the Blyvooruitzicht Plant, It would be of advantage, however, to ensure that the resin used possesses a stable, spherical and unfractured particle form.

4. Of the four resins tested, the Amberlite IRA.400 appears to be superior to the others. It has the highest capacity and reaction rate and is less susceptable to the polythionate poisoning than the others. After regeneration with Na_2S and HNO_3 it exhibits almost identical adsorbtion properties as the fresh resin.

The Ionac resin, although initially having as high a capacity and reaction rate as the Amberlite, deteriorates to a greater extent during operation. It was found to be impossible to restore the used Ionac to the same capacity as the fresh resin with the Na_2S regeneration.

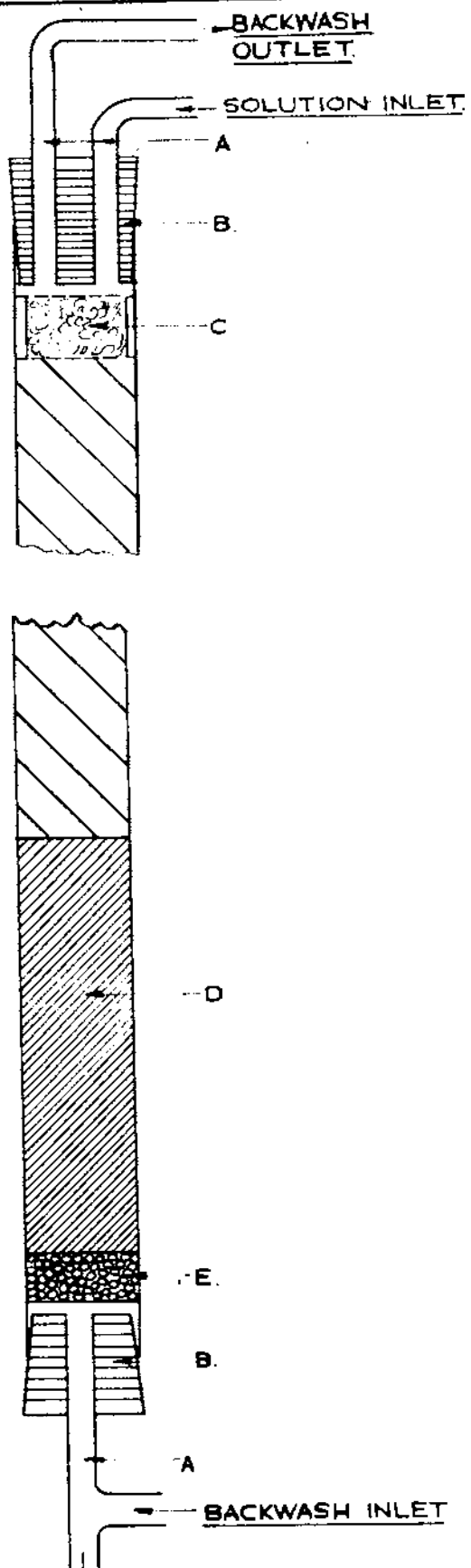
The Dowex I and Permutit resins have a lower initial capacity and inferior adsorbtion characteristics compared with the Amberlite, although possessing greater mechanical strength.

119/ APPENDIX

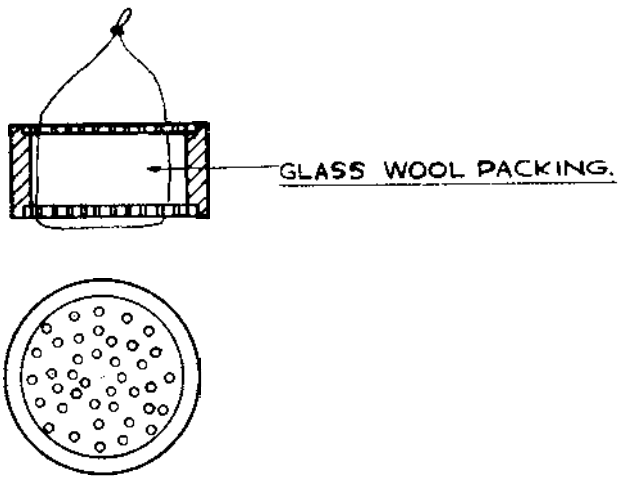
FIG. Nº 26.

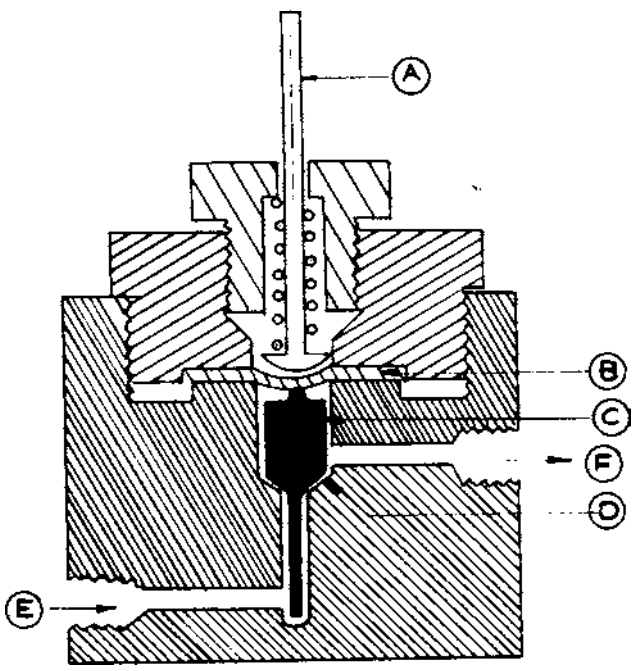
DETAILS OF LIFE TESTER COMPONENTS.

DETAILS OF RESIN COLUMN



DETAIL OF GLASS WOOL FILTERS.





DETAILS OF LIFE TESTER VALVES.

A. GLASS DELIVERY TUBES

B RUBBER STOPPERS

C. GLASS WOOL FILTER

D. RESIN.

E POROUS "CRACKERJACK BASE.

(A) SOLENOID OPERATED, SPRING LOADED PLUNGER.

(B) RUBBER GASKET

(C) HARD RUBBER VALVE.

(D) VALVE SEAT.

(E) SOLUTION INLET.

(F) SOLUTION OUTLET.

APPENDIX

SECTION B

DESCRIPTION OF THE LIFE TESTER AND METHOD OF OPERATION.

The resins under test were contained in 1" diameter glass columns. The height of the resin bed was approximately 10", the total height of the column being approximately 30", thus allowing adequate space for backwashing.

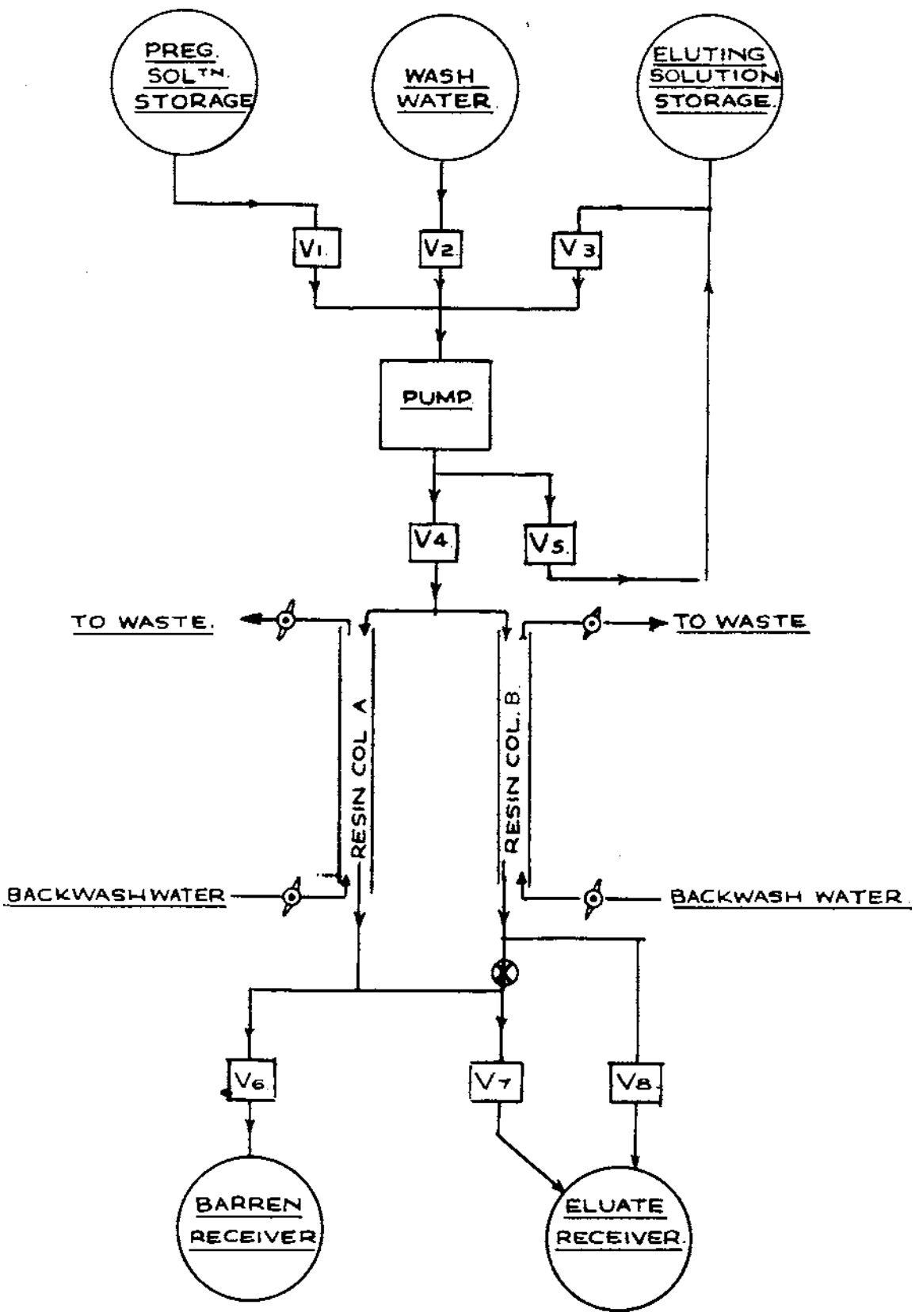
The various solutions were pumped from the rubber lined storage drums through $\frac{3}{8}$" Tygon tubing to the top of the column. Initially a glass tube inside the column carried the solution down the length of the free space above the resin to a distance 1" above the level of the resin bed, where it was evenly distributed over the whole column area. This internal delivery tube was later dispensed with, when it became apparent that, in the quantitative chloride capacity tests, errors were being introduced by the diffusion of chloride ions into the water in the free space above the resin bed. The various solutions were then distributed at the top of the column, which resulted in the complete displacement of any solution previously in the column. When it became apparent that resin losses during backwashing played an important part in the life of the resins, glass wool filters were fitted at the top of the column to act as a trap for the resin particles removed in the backwash effluent. These filters are illustrated in Figure No. 26, and by suitably packing the glass wool, it was found possible to prevent the coarser particles of resin being removed from the column, while at the same time permitting the passage of the very fine slime. The glass wool packing was replaced every 100 cycles and the entrapped resin replaced in the columns.

The solutions were pumped by a "Duplex Heavy Duty Chem-o-feeder" Diaphragm pump. This pump had two separate diaphragm

120/ mechanisms....

FIG. No. 27.

FLOW DIAGRAM FOR LIFE – TESTER.



mechanisms, each with inlet and outlet connections. When two resins were under test in the life tester, each outlet from the pump fed one column, and when four resins were under test, one pair of columns in parallel. The flow rate of the solutions could be controlled by adjusting the stroke length which permitted flow rates from 0 - 80 mls/min.

The correct flow of the various solutions was controlled by solenoid operated valves, the design of which is shown in Figure No. 26. These valves were made to operate in the correct sequence, corresponding to adsorbtion, washing and elution operations by a "Robotron" automatic timer. This instrument was designed to operate any six valves in any desired combination for a given period of time and then switching automatically to the next operation.

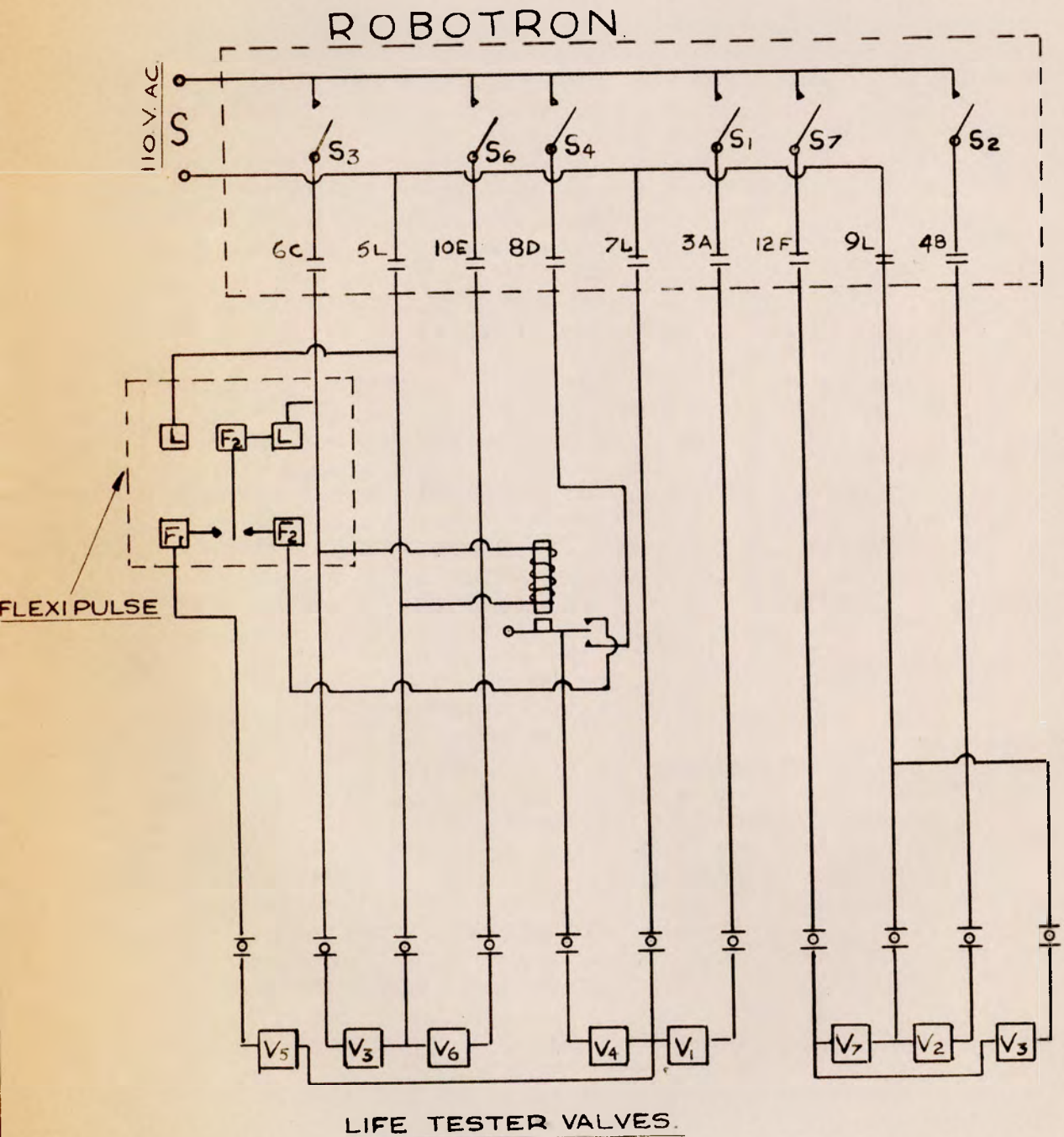
The elution operation required a flow rate very much smaller than that used in the adsorbtion or washing operations. To achieve this without altering the pump setting, a by-pass valve (V.5) from the pump outlet leading back to the eluting solution drum was included in the circuit. This valve was operated in conjunction with the valve (V.4) controlling the flow of solution to the columns, so that the eluting solution was alternatively pumped to the column and then back to the eluting solution storage drum. The timing of the opening and closing of these two valves was controlled by a "Flexipulse" switch which came into operation during the elution cycles. e.g. valve V.5 was open with valve V.4 closed for 30 seconds, followed by valve V.4 being open with V.5 closed for 10 seconds. In this way the eluting solution was pumped to the resin columns for only 10 seconds in 40, thus effectively reducing the flow rate to the columns to ¼ of that of the pump flow rate.

A study of Figures Nos. 27 and 28, which show the flow diagram and electrical circuit diagram employed on the life

121/ tester.....

FIG NO. 28.

SIMPLIFIED LIFE-TESTER CIRCUIT DIAGRAM.



LIFE TESTER VALVES.

tester will give a clear idea of the automatic operation of this instrument to simulate plant operating conditions.

It was not possible to include a backwashing operation in the automatic cycle since this required very careful adjustment of the flow rate to avoid resin losses. A manually operated backwashing system was included and this operation was carried out almost every day. In most cases the flow rate during backwashing was adjusted to give 100% bed expansion, and the washing continued until the effluent was reasonably free of slime. However on certain occasions a solid plug of material formed on top of the resin bed and this had to be broken up with a length of thin wire followed by alternate backwashes and downwashes in order to remove the accumulated slime.

The pregnant solution was clarified through a sand filter before being run into the 45 gal. pregnant solution storage drum. It was observed that after a few days standing in this drum a further amount of insoluble material separated from the solution and this caused a great deal of trouble by blocking the valves, the resin bed and the "cracker-jack" base supporting the resins in the columns.

During the normal operation the barren solution was discarded after neutralisation with lime.

The eluting solution after precipitation of the iron and Uranium was reacidified and returned to the eluting solution storage drum. In order to avoid either a decrease or increase in the total nitrate content of the solution, the following procedure regarding the recycling of the eluting solution was adopted. When approximately 20 gals. of the eluate had been collected, sufficient ammonia was added to bring the pH of the solution to a value of 7.0. The addition was made slowly and whilst stirring with the result that an easily settling precipitate was obtained. The solution was allowed to stand over-night

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and the clear supernatant liquor decanted off, filtered, and the volume measured. The requisite amount of nitric acid was then added to provide a 0.1N acid solution. The following calculation shows that this procedure provides an approximately constant composition of the eluting solution.

Consider a column of Amberlite IRA.400 containing 50 gms. of resin. In each elution cycle (50 x 3.6) milliequivalents of nitrate are adsorbed by this column, and consequently lost in the next adsorbtion operation. It has been found that for the complete elution of this column approximately 4 litres of a 0.1N HNO_3, 0.9N NH_4NO_3 solution are required, and approximately 200 mls. of water for washing after elution. Under these conditions the volume and concentration changes are as follows:

Nature of Eluting Solution	Vol.	Total Equivalents present			
		NO_3^-	NH_4^+	H^+	SO_4^{--}
Initial eluting solution	4.00	4.00	3.6	0.4	nil
Solution after passage through columns and including washings.	4.20	3.82	3.6	0.4	±.16
Solution after neutralisation of acid & pptn. of Fe^{+++} and UO_2^{++}.	4.20	3.82	4.0	nil	±.16
Solution after reacidification	4.20	4.24	4.0	0.42	±.16

Thus it can be seen that the nitrate concentrations of the re-cycled eluting solution remains constant at 1.0N. The NH_4^+, the SO_4^{--} concentration and the volume of the solution increase. It has been shown that the SO_4^{--} build up has no deleterious effect on the elution and the NH_4^+ and the volume increases are largely counterbalanced by adsorbtion losses in the ammonium uranate precipitate.

The re-cycling of the eluting solution was continued until it became contaminated in some way during the automatic operation. This was occasionally due to the incomplete closing

123/ of....

of the pregnant solution valve V.2, caused by the deposition of insoluble material on the valve seat which resulted in a leakage of the pregnant solution into the elution circuit. It was, however, found possible to recycle the eluting solution for as long as 200 cycles without any immediately apparent trouble. At one stage an attempt was made to use lime for the precipitation of iron, but this resulted in the deposition of calcium sulphate in various parts of the elution circuit causing an excessive amount of operational difficulties.

Chloride Capacity Tests.

The total chloride capacity of the various resin columns was measured as follows:

A 1.0N HCl solution was pumped through the columns at a flow rate of approximately 10 mls/min. This was continued until a chloride titration on the effluent gave an identical result to that on the influent. This usually occurred after the passage of approximately 4 litres of solution. The columns were then washed with water until the effluent contained no chloride. This step required a fairly large volume of water free from any anions such as SO_4'' or CO_3''. To provide this condition, tap water was passed through a column of the chloride form of Amberlite IRA.400 resin prior to its use in washing the columns on the life tester.

After washing, the chloride ion on the column was initially eluted with Chloride-free nitrate eluting solution. It was later suggested that this procedure might result in the formation of aqua-regia due to the high concentrations of NO_3' and Cl' inside the resin particles. Therefore, in later work, a sulphate solution consisting of 1.0N $(NH_4)_2SO_4$ and 0.5N H_2SO_4 was used to remove the chloride.

The elution was continued until no chloride was detectable in the effluent when the total volume was collected,

124/ measured....

measured and assayed for chloride by means of Volhard's method. The total amount of chloride in this effluent was taken to represent the chloride capacity of the column.

Loading Curves:

The loading curves were obtained by passing the particular pregnant solution through the column at a constant flow rate. Because of the pulsating nature of the flow provided by the diaphragm pump it was found necessary to introduce air into the free space above the resin bed in order to maintain a steady flow of solution through the resin bed.

The barren effluent was collected in 2 litre measuring cylinders. Samples of 50 mls. were taken for Uranium analysis every litre for the first three samples and thereafter every two litres. The loading was continued until approximately 30% adsorbtion had been reached.

For other tests a small sample of resin was removed from the column and was obtained by inserting a thin-walled glass tube of $\frac{1}{8}$" inside diameter into the column, and slowly forcing it through the resin bed when a small amount of the resin entered the tube at the different levels in the column. The top open end of the tube was then closed, the tube removed from the column and the resin sample washed into a sample bottle. When it was necessary to destroy the resin sample removed from the column an equal amount of fresh resin was substituted to maintain a constant column volume.

SECTION C.

STANDARD TESTS AND ANALYTICAL METHODS.

STANDARD TESTS AND ANALYTICAL METHODS

During the course of this investigation it was found necessary to develop methods for the measurement of various properties of the anion exchange resins of special interest to the extraction of Uranium. The significance of the various properties of the resins such as chloride and Uranium capacities has been discussed in a previous section. Attention will now be devoted to the experimental methods developed and used during this investigation.

It must be stressed, however, that the various standard tests and analytical methods described below were investigated only as far as was found necessary to ensure that they provided adequate and reproducible measurements of the particular property under investigation. Many improvements and simplifications will suggest themselves during the course of future resin work, but it is hoped that the methods described may form a basis of a standard system of analysis whereby the properties of the various new and used resins under investigation may be assessed.

PREPARATION OF SAMPLES, DRYING OF THE RESINS, AND THE BASIS FOR EXPRESSING EXPERIMENTAL RESULTS.

In most cases the resins as received were in a moist condition and contained a considerable amount of insoluble material adhering to them. Approximately 200 gms. of the resin were washed by agitation with distilled water and subsequent decantation of the supernatant liquid. This was continued until no further insoluble material appeared in the supernatant liquid.

The resins were then filtered on a Buchner suction flask, and spread out on a piece of blotting paper to remove as much as possible of the adhering water and while still moist, placed in an air tight bottle. Samples for analysis were taken by

126/ spreading.....

spreading out the resin on a non-adsorbent surface and removing small amounts from different parts of the resin.

Particular care was taken to avoid drying the resin prior to the measurement of capacities. Samples which had been dried before receipt were allowed to soak in distilled water for approximately three days before capacity measurements were made. Such precautions were considered necessary since it had been reported that a drop in capacity was observed after complete drying of the resin, the capacity being restored only after long periods of soaking in distilled water. The capacity tests described were designed so that the accurate dry weight of the resin could be obtained after the capacity had been measured.

Similar precautions were taken in the analysis of the resins for unstable compounds such as polythionates which were liable to decompose at high temperatures. In other cases, however, where the analysis involved the destruction or partial attack of the resin, samples were dried before weighing out the amount required for the analysis.

In order to obtain complete drying it was necessary to dry the resins in an air oven at 110°C. for 24 hours. This time could be considerably reduced by washing the resin with alcohol prior to drying. On exposure to the atmosphere the resins were found to readsorb moisture rapidly and for this reason all samples were cooled in a dessicator and weighed immediately.

The fundamental basis chosen for expressing analytical results was 1 gm. of chloride form resin dried at 110°C. for 24 hours. In many cases the conversion of the nitrate form resin to the chloride form resin prior to weighing introduced errors in the analysis due to the partial removal of the impurities

127/ to.....

to be determined. In such cases the resin was dried and weighed in the form received and a conversion factor, derived below, used to obtain the desired weight.

Consider 1 gm. of the resin as the free base.

Then: wt. of chloride form = $1 + \frac{c \times 35.5}{1000}$ gms.

wt. of nitrate form = $1 + \frac{c \times 62}{1000}$ gms.

$\therefore$ 1 gm. chloride form resin = $\frac{1000 + c \times 62}{1000 + c \times 35.5}$ gm. nitrate form

where c = capacity in milliequivalents/gm. of free base.

In the case of the Amberlite IRA.400 resin, where the capacity is 3.6 milliequivalents/gm. of dry RCl.

1 gm. chloride form resin = 1.085 gm. NO_3' form resin.

The error involved in considering the capacity in terms of gms. dry RCl instead of gms. of the free base is negligable.

Similar conversions can be applied for other forms of resin.

URANIUM AND CHLORIDE CAPACITY DETERMINATIONS

REAGENTS REQUIRED

(a) HCl solution. A 1.0N solution is required

(b) Pure Uranium sulphate solution. A solution of sufficient purity for this purpose was made by dissolving a high grade ammonium uranate precipitate in a slight excess of H_2SO_4 and neutralising with ammonia to a pH between 2 and 3. The concentration of Uranium is not critical but should be approximately 1.0 gm. U_3O_8/litre. There must be excess sulphate present, at least 3 mols. sulphate for every mol. of UO_2^{++}, i.e. approximately 1.0 gm/litre of sulphate.

Another more satisfactory method of preparing this solution was to boil an excess of the ammonium uranate precipitate with sodium carbonate, followed by filtration and neutralisation of the filtrate with sulphuric acid [a]. A slight excess of acid was then added and the solution boiled to expel CO_2. The free acid was then neutralised with ammonia and the pH of the

128/ solution

solution adjusted to a value between 2 and 3. In this way a concentrated stock solution was obtained which on dilution gave the required concentration of approximately 1.0 gm/litre U_3O_8 and approximately 1.0 gm/litre SO_4''.

The ammonium uranate should be as free of silica as possible, since large amounts of this element cause interference in the test, due to the adsorbtion as silicate anions on the resin.

(c) Nitrate Eluting Solution. A 1.0N NH_4NO_3 and a 0.5N HNO_3 solution was required. This reagent should be free of chloride.

Method

Approximately 2 gms. (4 mls.) of the resin are placed in a small glass column(b) The Uranium solution is passed through the resin bed at a flow rate of approximately two mls/minute. The passage of the solution is continued until the concentration of Uranium in the effluent is equal to the concentration in the influent solution. A convenient method for determining when the flow of solution should be stopped is to carry out a visual comparison of the colour developed by the addition of thiocyanate to the solutions. 1 ml. of the effluent and 1 ml. of the Uranium sulphate solution are placed in Nessler comparison tubes. To each is added 5 mls. of 50% NH_4CNS, 2 mls. of 20% HCl and 2 drops of fresh 10% $SnCl_2$ in 10% HCl. The two colour intensities are then compared and if no difference can be observed visually then the adsorbtion can be considered to be complete.

The resins are washed with distilled water(c) to remove any of the Uranium sulphate solution entrapped in the column, and then eluted with the 1.0N HCl solution. The effluent is collected quantitatively and the elution is continued until no more Uranium appears in the effluent(d). The column is then

129/ washed...

washed until no trace of chloride appears in the washings. The HCl effluent and washings are made up to a suitable volume in a standard flask and quantitatively analysed for Uranium(e), and the amount adsorbed on the column calculated.

The resin is then eluted with a nitrate eluting solution until free of chloride. The effluent is made up to a suitable volume, analysed for chloride and the amount of chloride adsorbed on the resin determined(f).

The resin is quantitatively removed from the column, filtered on a tared sinter glass curcible, and, if desirable, converted to the chloride form by washing with 20% HCl. It is then dried at 110°C. for 24 hours and weighed.

For comparison purposes a blank consisting of an approximately equal volume of the corresponding fresh resin can be run simultaneously under identical conditions.

The Uranium capacity is calculated in terms of gms U_3O_8/ gm. dry RCl, or as a percentage of the fresh resins capacity. The chloride capacity is most conveniently expressed in terms of milliequivalents chloride/gm. of dry RCl, or again as a percentage of the fresh resin's capacity.

NOTES:

(a) The Uranium and carbonate present in the filtrate correspond to the solubility of the complex $Na_4\{UO_2(CO_3)_3\}$. Addition of acid brings about the formation of Na_2SO_4 and UO_2SO_4 as follows

$$Na_4\{UO_2(CO_3)_3\} + 3H_2SO_4 = 2\ Na_2SO_4 + UO_2SO_4 + 3CO_2 + 3\ H_2O$$

so that on neutralisation 3 mols. of sulphate are present for every 1 mol. of UO_2^{++}.

(b) A convenient column can be made from a 50 ml. burette. The bottom of the burette is plugged with ½" of glass wool to act as a support for the resin.

(c) Prolonged washing of the resin should not be employed since uranium is removed from the resin by excessive amounts

130/ of.....

of distilled water. This is due in all probability to the dissociation of the uranyl sulphate complex.

$$UO_2(SO_4)_x^{(2x-2)-} \rightleftharpoons UO_2^{++} + xSO_4^{--}$$

which takes place on the resin. Two washes of 25 ml. have been found to be satisfactory.

(d) A simple qualitative test for the detection of the completeness of elution is to place 1 drop of 1% KI, and 1 drop of 1% $Na_2S_2O_3$ followed by 1 drop of 5% $K_3Fe(CN)_6$. If Uranium is present, a brownish-red colouration is obtained. It is important that the elution should not be carried much beyond the stage where Uranium just cannot be detected by the above spot test. Prolonged elution with HCl will bring about partial removal of certain of the poisons encountered on the ion exchange resins.

(e) Any of the standard methods for the determination of Uranium can be used. It has been found convenient, however, to dilute the eluate to 1 litre and determine the Uranium concentration by means of the thiocyanate method.

(f) The only method found to be suitable for the determination of chlorides in this solution is the Volhard method. Most of the adsorbtion indicators for detecting the silver chloride end point have been found to be unsatisfactory. Titration with mercurous perchlorate has also been found to be unsuitable.

EXPERIMENTAL RESULTS.

The effect on the Uranium capacity of the following factors was studied.

(a) The Effect of the Volume of Uranium Solution Used in Adsorbtio

Approximately 2.5 gms. of Amberlite IRA.400 resin were placed in a column approximately 1.0 cm. in diameter. A solution containing 1.00 gms. U_3O_8/litre, 3.40 gms. SO_4/litre and at a pH of 2.9, which was made as described above by dissolving ammonium uranate precipitate in H_2SO_4, was passed through

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FIG Nº 29 ADSORPTION OF URANIUM FROM SYNTHETIC SOLUTIONS.

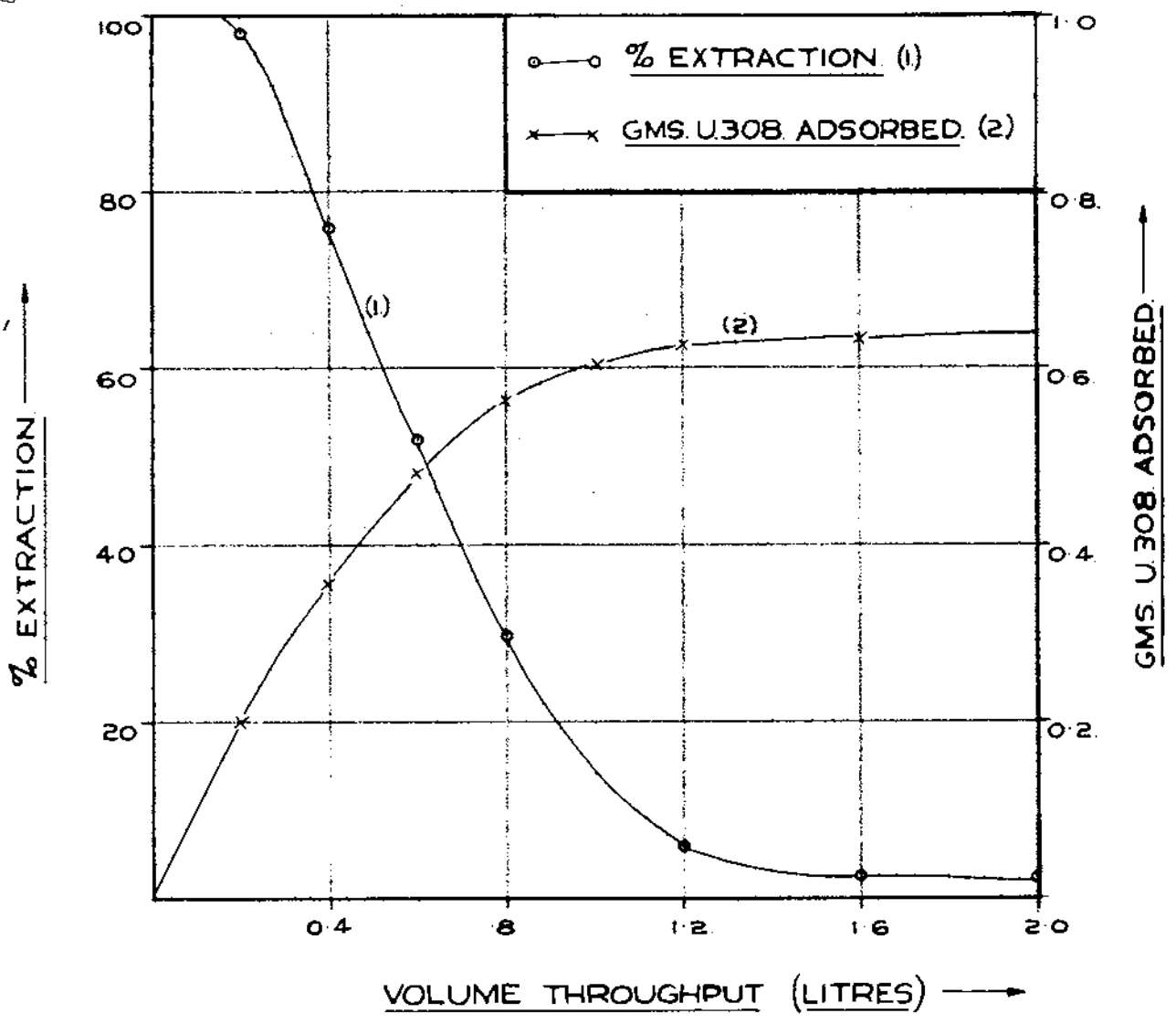
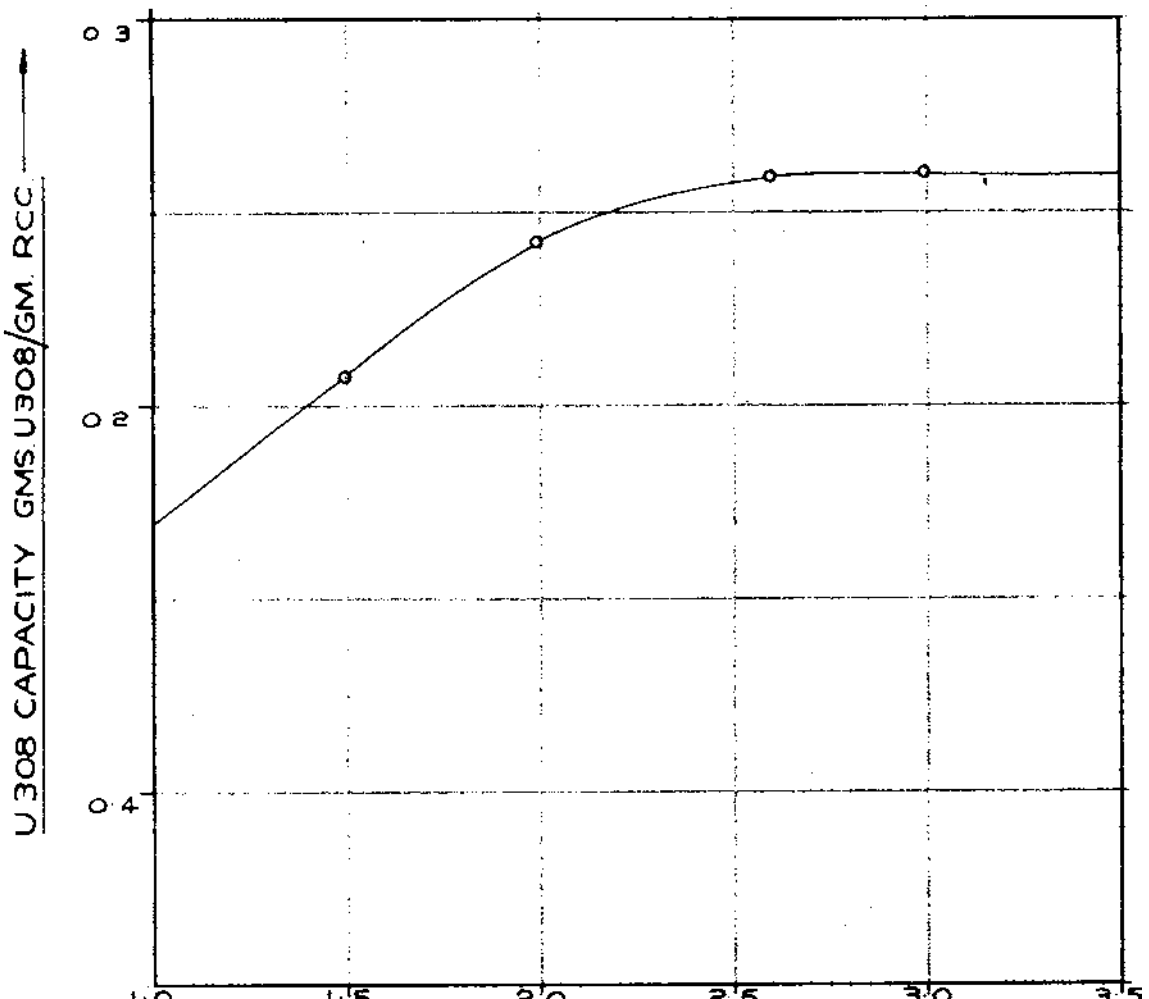


FIG. Nº. 30. EFFECT OF PH. ON THE ADSORPTION OF U308. FROM SYNTHETIC SOLUTIONS.



the column at a flow rate of 2 mls/min. Samples for analysis (5 mls.) were collected at 200 ml. volume intervals and analysed for Uranium.

The results are shown in Table No. 35, which provide data for the loading curve shown in Figure No. 29. By graphical integration, a graph of the amount of Uranium adsorbed against the volume was obtained as shown.

It can be seen that initially the amount of Uranium adsorbed increases rapidly, but after the passage of approximately 1.2 litres, the amount of Uranium adsorbed reaches an approximately constant value of 0.644 gms. This corresponds to a capacity of 0.262 gms U_3O_8/gm RCl, or 0.931 millimols of U/gm. RCl. The total chloride capacity of the resin was 316 milliequivalents/gm. RCl, so that the ratio

$$\frac{\text{total exchange capacity}}{\text{millimols Uranium adsorbed}} = 3.87$$

This suggests that the Uranium is adsorbed as a tetravalent anion, possible $\left(UO_2(SO_4)_3\right)^{''''}$.
This confirmed the suggestions made by R.L. Barnard[132] during the initial investigations on Uranium adsorbtion at the Massachusetts Institute of Technology.

However it was observed that the concentration of Uranium in the effluent from the column did not quite attain the value in the influent solution, but that a very slow adsorbtion of Uranium continued after this approximately constant value of 0.262 gms. U_3O_8/gm. RCl had been attained. Subsequent tests showed that after the passage of a large excess of solution for a period of 5 days, a constant capacity of 0.33 gms. U_3O_8/gms RCl could be obtained. This corresponded to 1.2 millimols Uranium per gm. RCl, which indicates the presence of a trivalent Uranium complex anion.

It seems likely, therefore, that the Uranium is initially adsorbed as a tetravalent anion, but that a slow reaction occurs whereby more Uranium is adsorbed and this anion changes to a

132/ trivalent.....

trivalent anion.

It is this initial rapid adsorbtion of the tetravalent anion which is of interest in the applications encountered in practice, and therefore the Uranium capacity test was designed to measure the capacity of the resin for this anion. It was concluded that large excesses of the Uranium solution should not be used nor should the adsorbtion be continued much beyond the stage where the initial adsorbtion is complete. At a flow rate of approximately 2 mls/minute, the difference in concentration between the effluent and the influent at this stage could not be detected by visual comparison of the thiocyanate colour and this method was used to determine when sufficient solution had been passed through the column.

(b) The Effect of the pH of the Uranium Solution.

The solutions containing 1.0 gms U_3O_8/litre and 3.5 gms sulphate/litre were adjusted to a series of pH values shown in Table No. 36 by the addition of ammonia or sulphuric acid. The Uranium capacities of samples of Amberlite IRA.400 were determined using these solutions as described in the method. The results are shown in Table No. 36 and graphically in Figure No. 30.

It was found that in order to obtain a maximum Uranium adsorbtion, the pH of the solution should be greater than 2.5 when a capacity of 0.259 gms U_3O_8/gm. RCl was obtained. At lower pH values, lower Uranium capacities were found. This was assumed to be due to the preferential adsorbtion of the bisulphate anion as illustrated in previous work by Barnard and Lower.[122,128]

At pH value above 3.5, the Uranium solution was found to contain traces of a gelatinous precipitate which caused blocking of the resin column. It was concluded, therefore, that the pH of the solution should lie between 2.5 and 3.5.

133/ TABLE NO. 35

TABLE NO 35

ADSORBTION OF U_3O_8 FROM SYNTHETIC SOLUTIONS OF URANIUM SULPHATE

Head Solution: U_3O_8 conc. - 1.00 g/l
SO_4'' " - 3,40 g/l
pH - 2.9
Wt. of resin (dry RCl) - 2.46 gms.
Flow rate - 2 mls/min.

Volume of Effluent	U_3O_8 conc. in Effluent	% Extraction	From graph. Wt. U_3O_8 adsorbed
0.2 litres	0.02 g/l.	98	0.200 gms.
0.4 "	0.24 "	76	0.360 "
0.6 "	0.48 "	52	0.485 "
0.8 "	0.70 "	30	0.565 "
1.0 "	-	-	0.605 "
1.2 "	0.94 "	6	0.624 "
1.6 "	0.97 "	3	0.636 "
2.0 "	0.98 "	2	0.644 "

TABLE NO 36

EFFECT OF pH ON THE ADSORBTION OF URANIUM FROM SYNTHETIC SOLUTIONS.

Head Solution: 1.0 gm U_3O_8/l. ± 3.5 g/l SO_4''
Flow rate 2 ml/min

pH	Uranium capacity of resin gms. U_3O_8/gm.
1.0	0.169
1.5	0.207
2.0	0.243
2.6	0.258
3.0	0.259

TABLE NO 37

EFFECT OF SO_4'' CONCENTRATION ON THE URANIUM CAPACITY

Head solution: 1.0 gm U_3O_8/l.
pH 2.9
Flow rate 2 ml/min

SO_4'' Conc.	Capacity
1.0 g/l	0.262 gms U_3O_8/gm
2.0 "	0.260 "
4.0 "	0.259 "
8.0 "	0.257 "

134/ TABLE NO 38

TABLE NO 38

EFFECT OF URANIUM CONCENTRATION ON RESIN CAPACITY

Uranium Conc.	Capacity
0.5 gms U_3O_8/l.	0.259 gms U_3O_8/gm.
1.0 "	0.259 "
2.0 "	0.260 "
5.0 "	0.265 "

(c) Effect of the Sulphate Concentration

A series of solutions containing 1.0 gms U_3O_8/litre and varying amounts of sulphate at a pH of 2.9 were prepared. The higher sulphate concentrations were obtained by addition of Na_2SO_4. The Uranium capacity of samples of Amberlite IRA.400 was determined using these solutions. The results are shown in Table No. 37.

It was found that over the range of sulphate concentration investigated, no significant change in capacity occurred with change in sulphate concentration.

G.W. Lower[128] found in his investigations that the amount of Uranium adsorbed decreased appreciably with increase in sulphate concentration of the solution. However, the synthetic solution used in his tests contained 0.5 millimols of Uranium while the sulphate concentration varied from 0 to 300 millimols. Under these conditions of large excesses of sulphate, this ion can be expected to compete successfully with the Uranium and thus bring about a decrease in Uranium adsorbed. The range covered in the experiments described above is 3.5 millimols of Uranium and from 10.4 to 83.4 millimols of sulphate per litre.

It can be concluded that over the range of sulphate concentrations encountered in the preparation of the Uranium solution, no significant change in the Uranium capacity of the resins occurred.

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(d) Effect of the Uranium Concentration

Solutions containing 0.5 to 5.0 gms U_3O_8/litre and 3.5 gms SO_4/litre at a pH of 2.9 were used to determine the capacity of samples of Amberlite IRA.400. The results are shown in Table No. 38.

No significant change in capacity was observed to occur with changes in Uranium concentration.

J.W. Lower[128] found that at low pH values (1.3) and high SO_4 concentrations, an increase in capacity occurred with increasing Uranium concentration. This is to be expected since the uranyl sulphate anion will, at high concentrations, compete more successfully with the bisulphate anion which is strongly adsorbed under these conditions. None of the capacities found by Lower was as great as the capacity determined in the above method.

It can be concluded that at high pH values between 2.5 and 3.5 no significant change in Uranium capacity occurs with changes in the Uranium concentration of the solutions.

(e) The Effect of Impurities:

It is convenient to prepare the Uranium solution from an ammonium uranate precipitate. This invariably contains Fe^{+++} and SiO_2 as impurities.

A study of the effect of these impurities was confined to an analysis of the HCl eluate after Uranium adsorbtion to determine to what extent these compounds were adsorbed. Although the influent solution contained these impurities, their presence could not be detected in the eluate and it was assumed that they were not adsorbed by the resin under the conditions of the test.

At a later stage it was observed that a certain Uranium solution deposited insoluble siliceous material on the resin and gave lower capacities than were anticipated. This phenomena was put down to be due to an abnormally high amount of silica

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in the Uranium solution. Nevertheless ammonium uranate precipitates containing as much as 15% SiO_2 have been extensively used for the preparation of the solution without anomalous results being obtained.

It is considered that the use of a reasonably pure Uranium precipitate as obtained on the plants may be used for the preparation of the Uranium solution without introducing serious errors.

137/ ANALYSES.....

ANALYSES OF THE RESINS FOR MOISTURE, ASH, SILICA, COBALT, IRON AND URANIUM.

METHOD:

(a) Moisture. Approximately 10-12 gms. of the moist resin sample are weighed into a tared moisture dish and dried at 110°C. for 24 hours. The sample is then cooled in a dessicator and weighed. The difference in weight represents the amount of water present.

(b) Total Ash. 1 - 2 gms. of the dried sample from (a) are weighed into a tared platinum crucible(a). The crucible is covered and slowly brought to a temperature of 400°C. over a period of two hours. This temperature is maintained for a period of one hour, after which time the lid is removed and the resin ignited at red heat with free access of air until constant weight is obtained(b). The crucible is cooled in a dessicator and weighed. The percentage ash can be calculated from the formula:

$$\% \text{ ash} = \frac{100a}{w}$$

Where a = Wt. of ash remaining in crucible
w = Original wt. of dry resin taken.

(c) Silica. The residue from (b) is moistened with 1 ml. of water followed by 1 ml. of hydrofluoric acid. After evaporation to dryness on a sandbath, a further 1 ml. of hydrofluoric acid is added and ½ ml. of 50% H_2SO_4 and the evaporation to dryness repeated. The crucible is heated to red heat for 30 minutes, cooled in a dessicator and weighed.

If b is the difference in weight of the crucible before and after this treatment, then

$$\% SiO_2 = \frac{100b}{w}$$

(d) Iron, Uranium and Cobalt. The residue from (c) is fused with 1 gm. of potassium pyrosulphate until a clear melt is obtained. After cooling, the cake is dissolved in hot water and the solution, after being made up to a definite volume in a

138/ standard....

standard flask, is analysed for Fe, U_3O_8 and Co.

If sufficient of these elements are present, standard volumetric or gravimetric methods can be used. Since in most cases only trace amounts of these elements are present, colourimetric methods are preferable, and have been found to give adequately accurate results even when large amounts are present. Suitable colourimetric methods for these analyses are :

Fe - o-phenanthroline method[8]
U_3O_8 - Thiocyanate colourimetric method[139]
Co - Nitroso - R - salt colourimetric method[90]

(e) Other non-volatile elements. The solution from (d) can be used for a qualitative examination for the presence of other suspected elements.

NOTES:

(a) If the resins are suspected to contain polythionates and other unstable sulphur compounds, the use of a platinum crucible is not recommended since bad staining and crystallisation of the platinum occurs. In such cases it is advisable to carry out the ignition in a glazed porcelain crucible, transferring the ash quantitatively to a tared platinum crucible for the silica determination.

(b) This procedure is essential since it has been found that a somewhat violent decomposition of the resin occurs on rapid heating which results in a loss of ash.

(c) If the determination of Fe and U_3O_8 is not required the pyrosulphate fusion can be eliminated. The addition of 1 ml. of 50% H_2SO_4 followed by gentle heating brings about satisfactory solution of the Co_3O_4.

ANALYSES OF THE RESINS FOR SULPHUR COMPOUNDS

(a) Total Sulphur

Originally this analysis was carried out according to Eschka's method,[21] but as the investigation into the nature of

these compounds progressed, a more accurate and quicker method was developed. This depends on the oxidation of these compounds with NaOBr and their subsequent determination as sulphate.

Reagents: NaOBr: Dissolve sufficient liquid bromine in 5% NaOH until the deep red colour of the bromine persists.

$BaCl_2$ solution: Dissolve 10 gms. of A.R. $BaCl_2$ in 100 mls. distilled water.

Method: Approximately 1 - 2 gms. of resin are boiled with 20 mls. of NaOBr in 100 mls. distilled water for one hour. A slight excess of HCl is added and the solution boiled until free of bromine.

The resin is filtered on a No. 541 Whatman's filter paper and washed twice with 5 ml. portions of 50% HCl, followed by three washes with distilled water.

The filtrate and washes are collected and made just alkaline with ammonia, diluted to approximately 250 mls., and made just acid with HCl. The solution is boiled and the sulphate precipitated with $BaCl_2$ in the usual manner. The resin is washed quantitatively into a tared sinter glass crucible, dried under suction and then for 24 hours at 110°C. and weighed.

$$\% \text{ Total Sulphur} = \frac{\text{Wt. of } BaSO_4 \times 0.1373}{\text{Wt. of resin}} \times 100$$

(b) Free of Colloidal Sulphur

Certain resin samples contain forms of sulphur soluble in CS_2. This has been assumed to be free or colloidal sulphur resulting from the decomposition of the polythionates on the resin. The following is the method used for determining this form of sulphur.

Method: 5 gms. of the air dried resin are weighed into a Soxhlet extraction thimble and extracted for 6 hours with re-distilled Carbon Disulphide in a Soxhlet extraction apparatus. The Carbon Disulphide extract is then evaporated to dryness on a water bath, and the residue oxidized with 20 mls. of a 10% Br_2

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solution in 10% HCl. The solution is boiled until clear, diluted to 250 ml. and the sulphate determined by precipitation with $BaCl_2$ in the usual manner.

(c) Tetrathionic Sulphur

The following method has been developed for the determination of the sulphur present on a fully eluted resin as the tetrathionate S_4O_6'' anion[a]

Reagents: NaOH solution: Dissolve 50 gms. of NaOH pellets in distilled water, cool, and make up to 500 ml.

H_2SO_4 solution: 125 mls. of C.P. sulphuric acid are diluted with distilled water, cooled and made up to 500 mls.

Formaldehyde solution: A concentrated 40% solution as obtained commercially is required.

Iodine solution: An accurately standardised iodine solution in potassium iodide is required.

Method: Approximately 5 gms. i.e. ± 10 ml. of the moist poisoned resin, are washed into a small column. The resin is eluted with the 10% NaOH solution, the eluate being collected quantitatively in a 500 ml. Philip's beaker. A flow rate of approximately 1 drop/second has been found suitable. After 200 ml. of the eluate has been collected, a clean beaker is placed to receive the eluate and the solution already collected is acidified with the sulphuric acid solution, 5 mls. of 40% formaldehyde added[b] and titrated with N/10 iodine to the first starch end point.

A further 100 mls. of the eluate are collected and treated as described above. This procedure is continued until a 100 ml. fraction of the eluate gives no further titration with iodine. Usually 300 mls. of eluate are sufficient.

The resin in the burette is then washed with water followed by 100 mls. of a 10% solution of HCl[c] and then washed quantitatively into a tared sinter glass crucible, dried at 110°C. for 24 hours and weighed.

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The percentage sulphur present as tetrathionate, S_4O_6'' is given by (a)

$$\%S = \frac{x}{w} \times 0.853$$

Where x = Total mls. of 0.100 N iodine required for the titration of the eluate.
w = Wt. of the resin.

NOTES:

(a) The reactions taking place on the resin in the case of the tetrathionate are as follows :

$$4S_4O_6'' + 6OH' = 5S_2O_3'' + 2S_3O_6'' + 3H_2O \quad - (A)$$

$$2S_3O_6'' + 6OH' = 4SO_3'' + S_2O_3'' + 3H_2O \quad - (B)$$

and combining (A) and (B)

$$2S_4O_6'' + 6OH' = 3S_2O_3'' + 2SO_3'' + 3H_2O \quad - (C)$$

Normally these reactions only take place in solutions at high OH' concentrations. However, when the tetrathionate is adsorbed on the resin, these reactions take place due to the adsorbtion of OH ions by the resin and the high concentration existing inside the pores of the resin. (See page 42.)

It can be seen that according to this reaction 8 gm. atoms of sulphur present as the tetrathionate give rise to the formation of 3 gm. mols. of S_2O_3''.

Thus from this reaction the equivalent weight of the S_4O_6 ions is 2/3 of its molecular weight.

i.e. 1 equivalent I_2 sol. $\equiv$ 2/3 x 1 gm. mol. S_4O_6

mls. of N/10 iodine $\equiv \frac{X}{10,000} \times \frac{8}{3} \times \frac{32}{1}$ gms. S.

$\therefore$ % Sulphur $= \frac{X}{w} \frac{8 \cdot 32 \cdot 100}{10,000 \cdot 3}$

$= \frac{X}{w} \times 0.853$

(b) The formaldehyde is added to remove the SO_3'' formed in reaction (C) by the formation of an aldehyde bisulphite. If colloidal sulphur is present on the resin, Na_2S is formed which causes interference in the titration. This can be removed in the alkaline solution by the addition of $ZnCO_3$ and filtration.

142/ (c) This....

(c) This operation is to convert the hydroxide form to the chloride form of the resin.

ANALYSIS OF THE RESIN FOR TOTAL NITROGEN

The Kjeldahl digestion method of analysis for total nitrogen has been successfully applied in the case of anion exchange resins.[21] The term "total nitrogen" excludes the nitrogen present on the resin as an adsorbed nitrate ion and, since this anion causes interference in the analysis, the nitrate eluted resin should be converted to the chloride form by washing with 100 mls. of 20% HCl prior to drying and weighing.

Method:

1 gm. of the dry chloride form resin is weighed into a Kjeldahl digestion flask. 10 gms. of potassium sulphate, and 30 mls. of conc. sulphuric acid are added in this order. The flask is covered with a loose fitting stopper and the mixture boiled until a clear solution is obtained. After cooling, this solution is transferred to an ammonia distillation flask. Sufficient NaOH is added to make the solution strongly alkaline together with a few zinc chips to prevent bumping. The flask is heated and the liberated ammonia determined by distillation into standard acid in the usual manner.

A blank determination on the reagents used must be carried out.

$$\text{milliequivalents Nitrogen/gm. dry resin} = \left\{ \frac{x - b}{w} \right\}$$

Where x = ml. N acid neutralized by sample

b = mls. N acid neutralized by "blank"

w = wt. of resin.

METHOD OF ANALYSIS FOR TETRATHIONATES IN PREGNANT AND ELUTING SOLUTIONS

One of the major difficulties encountered in the work on polythionates was the analysis of pregnant and eluting solutions for these compounds. The accepted method of determining the non-sulphate-sulphur by oxidation with bromine after sulphate removal with barium chloride proved to be unsatisfactory for trace amounts of polythionate in the presence of large amounts of sulphate. The initial precipitation and filtration of the barium sulphate from the large aliquots of solution required for the determination presented the major difficulty; particularly since the heating of these solutions had to be avoided due to the decomposition of the polythionates at high temperatures. Moreover, since the polythionates decompose in alkaline solution the removal of interfering ions such as Fe^{+++} and UO_2^{++} could not be accomplished by precipitation as the hydroxide.

The following colourimetric method for the determination of trace amounts of tetrathionates in pregnant and eluting solutions was developed. The method depends on the formation of thiocyanates with cyanide in just alkaline solutions according to the reaction :

$$S_4O_6'' + 3CN' + H_2O = S_2O_3'' + SO_4'' + SCN' + 2HCN \quad - \quad (a)$$

and subsequent determination of the thiocyanate by means of the ferric thiocyanate colourimetric method.

Reagents:

(1) Sodium Hydroxide Solution: Dissolve 20 gms. NaOH (chemically pure pellets) in 100 ml. distilled water, filter and cool.

(2) Sodium Cyanide Solution: Dissolve 5 gms. of fresh chemically pure sodium cyanide in 100 mls. of distilled water. The purity of the cyanide is important; the solution should give no cloudiness when acidified with HCl, and if allowed to stand for more than a few days should be tested before use.

(3) Hydrochloric Acid: Dilute 50 mls. of the C.P. acid to

144/ 100 mls....

100 mls. with distilled water.

(4) Ferric Chloride Solution: Dissolve 320 gms. $FeCl_3.6H_2O$ in water and dilute to 500 ml. Filter before use.

(5) Cation Exchange Resin: 5 to 10 ml. of a strong acid cation exchange resin are required for each determination. Amberlite IR.120 has been found to be suitable. The resin is converted to the hydrogen form by repeated washes with 10% HCl. 5 to 10 ml. are placed in a 1 cm. diameter glass column fitted with a tap. The resin can be regenerated after use for future analyses by washing with 10% HCl until free of Fe^{+++}.

Method:

Two 25 ml.(a) aliquots of the solution (one aliquot as a blank) are passed through approximately 10 ml. of the hydrogen form cation exchange resin. The amount of resin required and the flow rate depend essentially on the amount of iron and free acid present in the solution. For a typical pregnant solution containing, say, 2.5 gms. Fe^{+++}/litre and 2.0 gms. free H_2SO_4/l., 10 mls. of resin in a 1 cm. column will remove all the interfering cations at a flow rate of approximately 1 drop/second.

The sample is run to a level just above the resin bed and the column washed four times with 5 ml. portions of distilled water. The total volume collected should be kept to a minimum since the final volume after the addition of reagents should not exceed 100 ml.

After this treatment, the solution should be water white and possess no trace of cloudiness.

In the case of the one aliquot, referred to as the sample,(b) proceed as follows:

Add one drop of phenolphthalein indicator and make just alkaline with sodium hydroxide solution. Add 5 ml. of 5% NaCN solution, swirl and allow to stand for 10 minutes. Then add 5 ml. of 50% HCl solution and allow to stand after swirling for a few minutes. Add accurately 5 ml. of ferric chloride

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solution and make up the volume in a 100 ml. standard flask.

In the case of the second aliquot referred to as the blank[b] proceed as follows:

Add the same amount of sodium hydroxide as required in th the sample. Add 5 mls. of 50% HCl followed after a few minutes by 5 ml. of the 5% NaCN solution, followed after a few minutes more by 5 ml. of the ferric chloride solution. Make up to 100 mls. in a standard flask.

Should the solution be suspected to contain free cyanide, the HCl should be added before the NaOH solution in the case of the blank aliquot.

Filter the two solutions if necessary, and measure the transmittancy of the sample compared against the blank at 525mμ wave length.[c]

The standardisation curve relating the percentage transmission to the amount of tetrathionate in solution can be obtained by carrying out the above procedure (omitting the passage of the solution through the cation exchange resin) on aliquots of a pure standardised solution of sodium tetrathionate[d] The aliquots should be chosen so that they provide a range from 0 - 8 milligrams of sulphur as tetrathionate, which is the range that can be conveniently measured on 1 cm. and 2 cm. cells.

NOTES:

(a) The method as described permits sample aliquots of up to 50 mls. Larger volumes are not recommended since large amounts of cation exchange resin are then necessary to remove interfering cations, with the result that the displacement volume and the washing of the column necessitates making the final volume up to 200 ml. with consequent loss in sensitivity.

(b) This procedure of taking two aliquots and using one as a blank is necessary to eliminate interference from traces of thiocyanates often present in the pregnant solution. In effect

this method compares the ferric thiocyanate colour formed from both the tetrathionate and the thiocyanate originally present in the case of the sample, with only the thiocyanate originally present in the case of the blank. In the majority of the pregnant solutions only a trace of thiocyanate is present and the tetrathionate can be readily determined. If, however, much thiocyanate is present, this method, although theoretically still applicable, has not been found to be satisfactory. This is because the instrument used (the model DU Beckman Spectrophotometer) could only be adjusted to give 100% transmission with the blank in position if relatively wide slit adjustments were used. This gave a very broad wave length band which in turn introduced errors.

However, only in very exceptional cases was more than a trace of thiocyanate present in pregnant solutions.

(c) The percentage transmission should be measured within 30 minutes after the addition of the $FeCl_3$ to eliminate errors due to the fading of the ferric thiocyanate colour.

(d) The standardisation curve obtained for tetrathionates is virtually identical with the curve obtained for equivalent amounts of thiocyanate added to a ferric chloride solution according to reaction (a).

(e) A method for preparing pure sodium tetrathionate is given by Mellor.[75]

An accurate volumetric method of standardising this material is given by M. Goehring.[42]

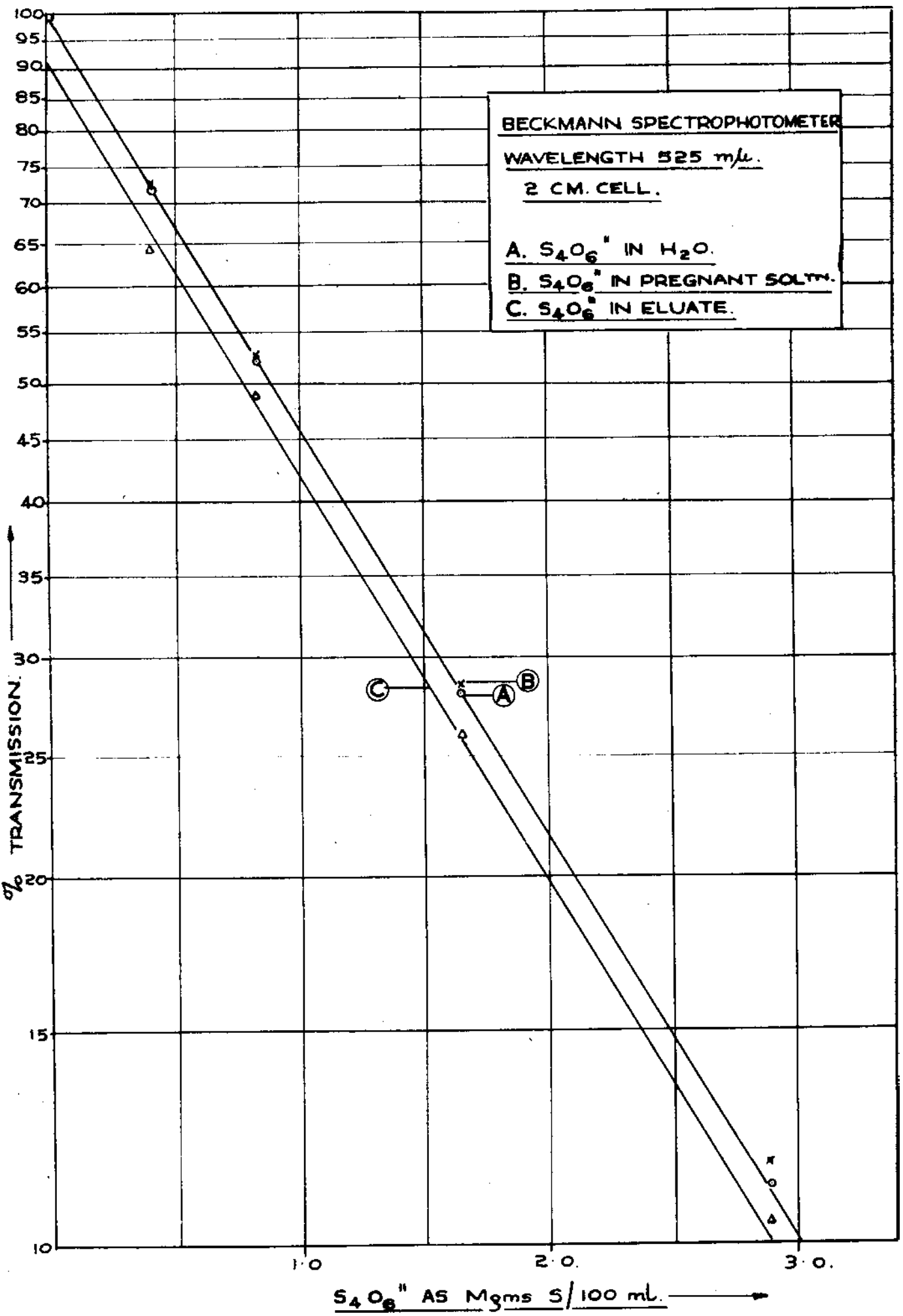
EXPERIMENTAL RESULTS:

(1) Preparation of Solutions of Known Polythionate Content.

Pure potassium tetrathionate was prepared by the method given by Mellor[75] from potassium thiosulphate and iodine. This salt was stored in a dessicator over conc. sulphuric acid. Analysis of the prepared $K_2S_4O_6$ (by the sulphite reaction

FIG Nº 31.

TRANSMISSION CURVES FOR TETRATHIONATE DETERMINATION.



recommended by Goehring) showed it to be 98.2% pure.

For these tests 0.1 gm. of $K_2S_4O_6$ were accurately weighed and dissolved in 100 ml. of water. 1 ml. of this solution contained 0.4128 mgms sulphur as tetrathionate. This solution was used immediately since the tetrathionate is unstable in aqueous solution and decomposes after a few days.

(2) Determination of the Standardisation Curve.

Volumes of the tetrathionate solution were added to the three different solutions as follows:

Solution (1) Tetrathionate added to water.

(2) Tetrathionate added to 10 ml. of pregnant solution

(3) Tetrathionate added to 10 ml. of eluate.

Solutions (2) and (3) were passed through the cation exchange column and treated as described in the method.

The following results were obtained:

ml. Polythionate added (0.4128 mgms S/ml.)	% Transmission 2 cm. cell 525 mμ		
	Solution No.		
	1. Water	2. Pregnant	3. Eluate
0	99.7	99.5	90.0
1 (0.413 mgms)	72.0	72.6	64.5
2 (0.826 ")	52.2	52.8	49.0
4 (1.651 ")	28.0	28.5	26.0
7 (2.89 ")	11.2	11.8	10.5

Plotting these results on semilogarithmic paper as shown in Figure 31, it was found that solutions (1) and (2) gave virtually identical straight lines passing through the 100% transmission point. Solution (3) gave a line parallel to the others but displaced through the 90% transmission point. A plant eluate was used in this solution and this discrepancy can be satisfactorily explained by assuming that a trace of tetrathionate was originally present in the plant eluate. In this case a line drawn parallel to that obtained but passing through the Y axis at 100% transmission would give a true representation of the

tetrathionate - percentage transmission relation. Such a line was found to be identical with that obtained in solutions (1) and (2).

(3) Effect of Various Factors on Transmission Values.

The effects of certain variations in the procedure described were studied as follows:

(a) Effect of allowing solutions to stand for various lengths of time after NaCN addition.

To 50 ml. of distilled water were added 2 mls. of the prepared tetrathionate solution (0.7270 mgms S), 1 drop phenolphthalein and 1 drop 20% NaOH until just alkaline. 5 ml. of 5% NaCN were then added and the solutions allowed to stand for varying lengths of time. After the elapse of the stated time, solutions were acidified with 5 ml. of 1:1 HCl solution, 5 ml. 40% $FeCl_3$ added and the volume made up to 100 ml. The percentage transmission was measured against a blank made up as described above, but omitting the addition of the tetrathionate.

Time of standing after NaCN addition in mins.	% Transmission 1 cm. cell
5	58.0
15	59.0
30	58.5
60	60.0
135	58.0

It may be concluded that the reaction between the tetrathionate and the cyanide is rapid and that the time of standing, provided it is more than 5 minutes, has but little effect.

(b) Effect of solution alkalinity

Tetrathionates react as follows in solutions of high alkalinity :

$$4S_4O_6'' + 6(OH)' = 5S_2O_3'' + 2S_3O_6'' + 3H_2O$$

The following results showed that the above reaction does not occur if small excesses of NaOH are added to the

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solution prior to the NaCN addition.

ml. Tetrathionate solution added	% Transmission 1 cm. cell	
	Solution just alkaline	2 ml. 20% NaOH added in excess
1	66.6	66.7
2	49.1	48.8
4	25.8	25.9
7	10.3	10.5

The tetrathionate solution contained 0.8256 mgms S/l.

(c) The effect of the acid added.

The effect of the addition of different amounts of HCl to the solutions prior to the addition of $FeCl_3$ is shown below.

ml. Tetrathionate solution added.	% Transmission 1 cm. cell		
	1 ml. 1:1 HCl	3 ml. 1:1 HCl	5 ml. 1:1 HCl
1	66.6	67.7	68.5
3	34.4	36.2	37.5
5	19.0	19.7	20.2
7	10.6	11.2	11.6

It will be seen that the greater additions of acid resulted in a slightly higher percentage transmission. However, with the smaller quantities of acid, a blue precipitate (presumably ferric ferrocyanide) formed on the addition of $FeCl_3$. This necessitated laborious filtration prior to the transmission measurement. Thus the higher acid concentration was preferred.

(d) The effect of filtration of the solution prior to colour measurement.

The formation under certain conditions, of a blue precipitate on addition of $FeCl_3$ to the solutions suggested that the filtration of even an apparently clear solution would result in different transmission values. The following results showed that this was not the case.

mls. Tetrathionate solution added	% Transmission 1 cm. cell	
	Solution filtered	Solution unfiltered
0	98.0	98.1
1	70.8	70.9
2	51.9	51.4
4	27.8	27.2
7	11.1	11.0

(e) The effect of adding varying amounts of NaCN solution

In view of the possible formation of ferric ferrocyanide it was thought desirable to omit the addition of NaCN to the blank aliquots. The results below, however, show that the NaCN exhibits a slight adsorbtion at the wave length used. Thus in accurate work the NaCN addition should be made to the acidified blank.

mls. 5% NaCN added	% Transmission 1 cm. cell	
	Solutions compared with blank containing no NaCN	Solutions compared with blank containing same amts. NaCN
1	37.9	37.9
3	37.6	37.9
5	37.2	37.9
10	36.9	37.9

(f) The effect of fading of the ferric thiocyanate colour and other variables.

No quantitative determinations were carried out but it was observed during the course of many analyses that a slight increase in the percentage transmission occurred after ½ hour standing. This was assumed to be the result of the fading of the ferric thiocyanate colour as observed by other investigators.

For other variables such as the wave length, the recommendations of other investigators into the measurement of the ferric thiocyanate colour were adopted.

(4) Limitations of Method:

This method has been found to be satisfactory for analyses of pregnant solutions and eluates containing only small amounts of thiocyanates. Large amounts of thiocyanates

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and substances such as sulphides, which form thiocyanates with NaCN, interfere.

Polythionates, other than the tetrathionates, give similar reactions with cyanide, but depending on the nature of the polythionate different amounts of thiocyanate are formed. Thus complex mixtures of the various polythionates cannot be determined by this method alone. However, it appears reasonably certain that the polythionate present in pregnant and eluting solutions is the tetrathionate in which case this analysis is directly applicable.

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METHOD OF ANALYSIS FOR COBALTICYANIDE IN PREGNANT AND ELUTING SOLUTIONS

A method of analysis for traces of cobalticyanide anion in pregnant and eluting solutions was required. These solutions contain large amounts of Fe^{+++}, UO_2^{++} and in the case of the pregnant solutions, comparatively large amounts of Co^{++}. The amount of cobalticyanide present seldom exceeded 0.005 gms/litre. Complete precipitation of these minute quantities of cobalticyanide by means of insoluble metallic salts proved to be impossible.

A sensitive colourimetric method for determining cobalt was available[a] and the problem of the analysis was the separation of the cobalticyanide from the cationic cobalt and other impurities. This was achieved by the use of ion exchange resins in two ways as described below :

METHOD (A) For samples containing more than 1 mgm. Co/l.

An aliquot of solution, not exceeding 50 mls.[a] was passed through 10 mls. of Amberlite IR.120 cation exchange resin to remove all the impurities. The column of resin was washed four times with 10 ml. portions of distilled water. The effluent and washings which contained no interfering cations were collected in a 500 ml. Philip's beaker.

10 ml. of 50% H_2SO_4 were added and the solution evaporated to dense white fumes of SO_3 to decompose the cobalticyanide. After cooling, 1 ml. of conc. HNO_3 and 1 ml. of sulphuric-perchloric acid mixture were added and the solution evaporated to complete dryness.

The cobalt in the residue was then determined by the nitroso-R-salt method[a].

METHOD (B) For samples containing less then 1 mgm/l.

Two anion exchange columns each containing approximately 2 gms. Amberlite IRA.400 were set up so that the effluent from the first column (A) passed through the second column (B) [6]

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A suitable aliquot of the solution was passed through the two columns in series at a flow rate not exceeding $\frac{1}{2}$ ml/min/sq. cm. The columns were then washed three times with 50 ml. portions of distilled water.

The resin was removed quantitatively from each of the two columns and filtered separately through a No. 541 Whatman's filter paper. The resins were ashed in porcelain crucibles and the ash fumed to dryness with 10 mls. 50% H_2SO_4 as described in Method (A). The cobalt in the residues was then determined by the Nitroso-R-salt method(a). In the majority of cases the residue from the column A contained all the cobalt and when a large amount appeared in B the analysis was repeated with approximately larger volumes of resin in column A.(b)

NOTES:

(a) The nitroso-R-salt colourimetric method requires a sample containing from 0.05 to 0.30 mgms of cobalt. Larger volumes than 50 ml. should not be taken since excessively large columns of the cation exchange resin are then required. For method see ref. 90.

(b) This procedure is essentially to ensure that all the cobalticyanide anions are adsorbed from the pregnant solution by the anion exchange resins. In Method A it is safe to assume that if no iron appears in the effluent, all the other cations have also been removed. No such simple test is possible to ensure that sufficient resin has been used in Method B.

COMPARISON OF METHODS:

Of the two methods described, Method A was preferred for the analysis of cobalticyanide in solutions containing more than 1 mgm Co/l. This method possesses the important advantage that all the cations such as Fe^{+++} and Mn^{++} which interfere in the Nitroso-R-salt method are eliminated. Interfering anions

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GENERAL SUMMARY

Investigations have been carried out into the life of various Anion Exchange Resins employed on the Rand for the extraction of uranium from the uranium Leach Liquors.

It was found that in the case of the leach liquors produced at the Western Reefs Pilot Plant, and at the West Rand Consolidated Uranium plant, the major factor causing a decrease in the efficiency of the Ion exchange resins was the presence of certain chemical poisons in these pregnant solutions. These poisons were identified as the Cobalticyanide Anion $Co(CN)_6'''$ and the Tetrathionate anion S_4O_6''. Both these compounds are derived from cyanidation of the ore for gold extraction prior to the uranium leach. The cobalticyanide is formed during the cyanidation, and also in certain cases during the addition of a recycled Manganese Dioxide slurry containing cobalt to the slightly alkaline cyanide residue, containing traces of cyanide anions. The tetrathionate is formed by the oxidation of thiocyanate anions, formed during cyanidation, by the acid oxidizing conditions obtained in the uranium leach. The amount of these compounds appearing in the pregnant solutions can be considerably reduced by the thorough washing of the cyanide residue prior to the uranium leach.

Of these two chemical poisons, the cobalticyanide anion is the most serious. Although generally present in smaller concentrations than the tetrathionate anions, it is strongly adsorbed by the resin, and once adsorbed is

extremely.....

extremely difficult to remove. It therefore constitutes a serious cumulative poison. The tetrathionate anion on the other hand, although strongly adsorbed, is partially removed by the acid nitrate eluting solution, and can also be completely removed by regeneration procedures such as treating the poisoned resin with 30% NaOH or 5% NaSH. A method was developed for the removal of cobalticyanide from the poisoned resins by means of hot 50% NH_4CNS, but this was not economic on a large scale. Therefore several alternative methods were discussed with a view to the elimination of the cobalticyanide anions before coming into contact with the Ion exchange columns.

Experiments were also conducted on the life of various resins operating on pregnant solutions produced at the Blyvooruitzicht Pilot Plant.

In these solutions the amounts of the poisons were very small and did not constitute a major consideration in the life of the resins. In this case a detailed study was made of the resin losses likely to occur due to the disintegration and subsequent removal of the fine resin particles during the backwashing operations. It was found that by taking certain precautions, these losses could be reduced to a minimum, so that no special consideration need be devoted to the production of a resin with an exceptionally high abrasion resistance.

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REFERENCES

1. Ackerman A. Bull. Soc. Chim. France, 1947. 619

2. Adams B.A. & Holmes E.L. J. Soc. Chem. Ind. 54 1 - 6T 1935.

3. Albanese A.A. & Frankston J.E. Biol. Chem. 159, 185, 1945.

4. Anon. Forecast 10 243 1948.

5. Anon. J. Soc. Them. Ind. P.339 Dec., 1945.

6. Applebaum S.B. J. Am. Waterworks Assoc. 30 1938.

7. Archibald R.M. J. Biol. Chem. 156 1 121, 1944.
and 159 693, 1945.

8. A.S.T.M. Methods 1950. P.328.

9. Austin P.R. U.S. Pat. 2,316,315. 1943.

10. Barrer R.M. "Diffusion in and Through Solids" Cambridge University Press. 1941

11. Bauman W.C., Skidmore J.R. & Osmun R.H. Ind. Eng. Chem. 40 1350, 1949.

12. Bauman W.C. & Eichhorn J. J. Am. Chem. Soc. 69 2830, 1947.

13. Bauman W.C. "Ion Exchange Theory & Application" Ed. by F.C. Nachod. N.Y. Acad. Press, 1949.

14. Beaton R.H. & Furnass C.C. Ind. Eng. Chem. 33 1501, 1949.

15. Bendall J.R., Partridge S.M. & Westall R.G. Nature 160 374, 1947.

16. Block E. & Ritchie R.J. Ind. Eng. Chem. 39 1581, 1948.

17. Block R.J. Chem. Revs. 38 501, 1946.

18. Boyd G.E., Adamson A.N. & Myers L.S. J. Am. Chem. Soc. 69 2836, 1947.
and 72 4807, 1950.

19. Boyd G.E., Schubert J. & Adamson A.N. J. Am. Chem. Soc. 69 2818, 1947.

20. Boyd G.E. Am. Rev. Phys. Chem. 2 309, 1952.

21. British Standard Methods No. 1016, 43, 1946.

22. Buck, R.E. & Mottern H.H. Ind. Eng. Chem. 37 635, 1945.

23. Burrell, H. Ind. Eng. Chem. 30 358, 1938.

24. Cerecedo, L.R. & Hennessy, D.J. J. Am. Chem. Soc. 59 617, 193

25. Challenor, S.W., Kieser, N.E. & Pollard A. Nature 161, 1023, 1948.

26./

26. Cheetham, H.C. & Myers, R.J. U.S. Pat. 2,341,907. 1944.

27. Cleaver, C.S., Hardy R.A. & Cassidy, H. J. Am. Chem. Soc. 67 1343, 1945.

28. Cohn, W.E. Science 109 377, 1948.

29. Collins, L.F. J. Am. Waterworks Assoc. 29 1472, 1937.

30. Cole, G.M. U.S. Pat. 2,253,061, 1940.

31. Cranston, H.A. & Tomson, J.B. Ind. Eng. Chem. Anal. Ed. 18 5, 323, 1946.

32. D'Alelio, G.F. U.S. Pat. 2,208,172. 1940.

33. Dubnoff, J.N. J. Biol. Chem. 141 711, 1941.

34. Eastmond, E.J. J. Optical Soc. 36 1, 47, 1946.

35. Elmore, D.T. Nature 161, 931, 1948.

36. Englis, D.T. & Fiess, H.A. Ind. Eng. Chem. 36 604, 1944.

37. Evans, B.S. & Higgs, D.G. Analyst, 70 158, 1945.

38. Furnass C.C. & Beaton, R.H. Ind. Eng. Chem. 33, 1500, 1949.

39. Glueckauf, E. Nature 166, 775, 1950.

40. Glueckauf, E. & Duncan Nature 167 713, 1951.

41. Glueckauf, E. Endeavour 10 40, 1950.

42. Goehring, M. Z. Anal. Chem. 128 6-9, 1947.

43. Gregor H.P. J. Am. Chem. Soc. 70 1293, 1948.

44. Gregor, H.P. & Bregman, J.I. J. Am. Chem. Soc. 70 2370, 1948.

45. Grehe, J.J. & Bauman, W.C. U.S. Pat. 2,387,898, 1945.

46. Griesbach, R. Angew. Chem. 52 215, 1939.

47. Gustafson, H.B. Ind. Eng. Chem. 41 464, 1949.

48. Hamer, P. Ind. Chemist. 24 362, June, 1948.

49. Harris, R.J.C. & Thomas, J.F. Nature 161 931, 1948.

50. Hems, B.A., Page, J.E. & Waller, J.C. J. Soc. Chem. Ind. 67 77, 1948.

51. Hochberg, M., Melnick, D. & Oser, B.L. J. Biol. Chem. 158 265, 1945.

52. Hopkins, S.J. Mfg. Chemist, 17 285, 1946.

53. Hunter, M.J. & Bauman, W.C. U.S. Pat. 2,409,861, 1946.

54. Jenny, H. J. Colloid Science, 1 33, 1946.

55. Jenny, H. J. Phys. Chem. 36, 2217, 1932.

56. Juda, W. & Carron, M. J. Am. Chem. Soc. 70 3295, 1948.

57./

57. Kressman, T.R.E. & Kitchener, J.A. J. Chem. Soc. 72 1208 1949.

58. Kunin, R. Anal. Chem. 21 87, 1949.

59. Ibid. 22 64, 1950.

60. Kunin, R. Ind. Eng. Chem. 42 65, 1950.

61. Kunin, R. & McGarvey, Ind. Eng. Chem 41 1265, 1950.

62. Kunin, R. & Myers, R.J. "Ion Exchange Resins". John Wiley & Sons. 1950. Chap. IV P.51. Etseq.

63. Kunin, R. & Myers, R.J. Far. Discussions. No. 7 114, 1949.

64. Kunin, R. & Myers, R.J. J. Am. Chem. Soc. 69 2874, 1947.

65. Kunin, R. & Myers, R.J. J. Phys. & Coll. Chem. 51 5, 1947.

66. Levesque, C.L. & Craig, A.M. Ind. Eng. Chem. 40 96, 1948.

67. Lindsay, F.K. & D'Amico, J.S. Ind. Eng. Chem. 43 1085, 1951

68. Lyman, J.F., Browne, E.H. & Otting, H.E. Ind. Eng. Chem. 25 1297, 1933.

70. Martin, A.J.P. & Synge, R.L.M. Bio Chem. J. 35 1358, 1941.

71. Matchett, J.R., Legoult, R.R., Nimimo, C.C. & Notter, G.K. Ind. Eng. Chem. 56 851, 1944.

72. Mottern, H.H. & Buck, R.E. U.S. Pat. 2,445,583, 1948.

73. Mayer, W. & Tompkins, E.R. J. Am. Chem. Soc. 69 2866, 1947.

74. McBurney, C.H. U.S. Pats. 2,591,573, 2,591,574. 1952.

75. Mellor, J.W. "Comp. Treatise on Inorganic & Theoretical Chem." 10 (S, & Se.) Longmans, Green & Co. Ltd.

76. Michaels, A.S. Ind. Eng. Chem. 44 1923, 1952.

77. Morris, J.C. & Carritt, J.V. J. New Engl. Waterworks Assoc. 62, 1, 1948.

78. Myers, R.J. & Eastes, J.W. Ind. Eng. Chem. 33 1303 1941.

79. Myers, R.J. Ind. Eng. Chem. 35 3, 859, 1943.

80. Myers, R.J. & Eastes, J.W. & Urquhart, D. Ind. Eng. Chem. 18 447, 1941.

81. Nachod, F.C. "Ion Exchange, Theory & Application" N.Y. Acad. Press, 1949.

82. Nachod, F.C. & Wood, W. J. Am. Chem. Soc. 66 1380, 1944.

83. Nees, A.R. & Bennett, A.N. U.S. Pat. 2,375,165. 1945.

84. Newkirk, T.H. & Handleman, M. Ind. Eng. Chem. 41 452, 1949.

85. Olson, H.M. J. Am. Waterworks Assoc. 40 301, 1948.

86. Osmun, R. & Wirth, L. Ind. Eng. Chem. 43 1076, 1951.

87. Oxford, W.F. Jr. U.S. Pat. 2,437,475. 1945.

88. Pemberton, R.T. & Holmes, E.L. Brit. Pat. 601,321 1948.

89. Permutit Co. Brit. Pat. 490,704, 490,799. 1938.

90. Pinkney, E.T., Young, R.S. & Dick, R. Ind. Eng. Chem. Anal. Ed. 18 474, 1946.

91. Riches, J.P.R. Nature. 158 96 1946.

92. Rieman, W. "Ion Exchange, Theory & Application" Ed. by F.C. Nachod, N.Y. Acad. Press. 1949.

93. Riley, F.R. & Day, H.M. Chem. Eng. Prog. 44 353, 1948.

94. Rohm & Haas Co., Phil. "Amberlite Ion Exchange Resins" Tech. Bulletin.

95. Schubert, J. J. Phys. & Coll. Chem. 53 340, 1948.

96. Schubert, J. & Richter, J.W. J. Phys. & Coll. Chem. 52 350, 1948.

97. Schubert, J. & Richter, J.W. J. Am. Chem. Soc. 70 4259, 1948.

98. Schubert, J., Boyd, G.E. & Adamson, A.W. J. Am. Chem. Soc. 69 2818, 1947.

99. Sillen, G.L., Ekedahl,E. & Hogfeldt, E. Nature 166 722, 1950.

100. Spaulding, C.H. Public Works 77 27, 1946.

101. Sperber, E. J. Biol. Chem. 166 1, 75, 1946.

102. Sussman, S. U.S. Pat. 2,442,989. 1948.

103. Sussman, S., Nachod, F.C. & Wood, W. Ind. Eng. Chem. 37 618, 1945.

104. Tendeloo, H.J.C. Disc. Far. Soc. 1 295, 1947.

105. Thomas, H.C. J. Am. Chem. Soc. 66 1664, 1944.

106. Thomas, H.C. Ion Exchange Theory & Application, Ed. F.C. Nachod, N.Y. Acad. Press, 1949.

107. Tomkins, E.R. & Meyer, S.W. J. Am. Chem. Soc. 69 2859, 1947.

108. Tomkins, E.R., Khym, J.X. & Cohn, W.E. J. Am. Chem. Soc. 69 2769, 1947.

109. Tomkins, E.R. Anal. Chem. 22 1354, 1950.

110. Treadwell, F.P. & Hall, T.H. "Analytical Chemistry" 1 (qual.)

111. Whitehorn, J.C. J. Biol. Chem. 56 751, 1923.

112. Ibid. 108 633, 1935.

113. Wheaton, R.M. & Bauman, W.C. Ind. Eng. Chem. 43 1088, 1951.

114./

114. Wiegner, G. & Jenny, H. Colloid Z. 43 268, 1927.

115. Wieland, T. Berichte 77 539 - 541, 1944.

116. Winters J.C. & Kunin, R. Ind. Eng. Chem. 41 460, 1950.

117. Winters, J.C. Chem. Ind. 62 754, 1948.

118. Wiklander, L. Ann. Roy. Agr. Col. Swed. 14 1, 1946.

REFERENCES (Continued)

SECRET REPORTS

These reports are available for consultation at the Government Metallurgical Laboratory, Johannesburg.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

Topical Reports MITG A Series.

119. MITG A 64 "Experiments on Rand Leach Liquors with Cation Exchange Resins." N.N. Schiff. 1949.

120. A 93 "Removal of Uranium From Rand Leach Liquors With Anion Exchange Resins." N.N. Schiff. July, 195

121. A 96 "Removal of Uranium From Rand Leach Liquors With Anion Exchange Resins. II. Tests with Process X Liquors". S. Bailey. July, 1950.

122. A 97 "Preliminary Study of the Adsorbtion of U^{++++} and Other Metallic Ions by Anion Exchange Resins." R.L. Barnard. August, 1950.

123. A 100 "Recovery of Uranium From Rand Gold Ores" R.D. McDonald Et Al.

124. A 101 "Adsorbtion of Uranium From Leaching Residue Pulps by Anion Exchange" F.N. Oberg, 1951.

125. A 102 "Removal of Uranium From Rand Leach Liquors With Anion Exchange" Part III. Cyclic Tests With X and Y Process Leach Liquors obtained by Filtration. N.N. Schiff. February, 1951.

126. A.105 "Removal of Uranium From Rand Leach Liquors With Anion Exchange Resins" Part IV. Cyclic Tests with X Process Leach Liquors Obtained by Thickening. N.N. Schiff.

127. A 107 "Removal of Uranium From Rand Leach Liquors With Anion Exchange Resins. Part V. Further Studies on Process Solutions" N.N. Schiff, March, 19

128. A 108 "Systematic Ion Exchange Studies." G. Lower. 1951.

REFERENCES (Continued)

CHEMICAL RESEARCH LABORATORY

D.S.I.R. Great Britain

Report Series CRL/AE

129. CRL/AE 77 "Use of Anion Exchange Resins in Treatment of X ore Leach Solutions." T. Harbutt & G.L. Hilward. March. 1951.

130. 82 "Preliminary Account of the Use of Ion Exchange Resins for the Recovery of Gold From Cyanide Solutions." Forrest Et Al. Sept., 1951.

131. 90 "Further Investigations Into the Use of Anion Exchange Resins for the Recovery of Gold From Cyanide Solutions."

132. 94 "Effect of Various Anions on the Adsorbtion of Uranium by Anion Exchange Resins." Part II. F. McClone & G.L. Hilward. June, 1952.

REFERENCES (Continued)

GOVERNMENT METALLURGICAL LABORATORY

PROGRESS REPORTS

Series Leaching.

133. P.R. No. 42 "Recovery of Uranium From Western Reefs Pregnant Solutions by Anion Exchange" R.S. Olson, March, 19

134. No. 59 "Operation of the Special Investigation Plant at Blyvooruitzicht." H. Bath. May, 1951.

135. No. 79 "Report Covering Operations of the Western Reefs Pilot Plant for period 24th June - 16th August, 1951". J. Ferguson.

136. No. 83 "Operations of Western Reefs Experimental Plant. Small Scale Tests to Determine H_2SO_4 Consumptions and MnO_2 Additions for Special two Stage Leaching." P. Lambert, January, 1952.

137. No. 87 "Operations of the Western Reefs Experimental Plant for Period 17th August - 22nd December, 1951" J. Ferguson. March, 1952.

138. No. 89 "Blyvooruitzicht Gold Mining Co. Ltd. Double Leach". H. Bath. March, 1952.

Series Analytical

139. "Determination of Uranium in Plant Solutions. Thiocyanate Method" T. Steele & F. Coetzee. August, 1951.

Miscellaneous Reports

140. "Preliminary Anion Exchange Tests on Western Reefs Pregnant Solutions" T.V. Arden, R.S. Olson, T.J. Brunner & R.D. McDonald.

141. "Preliminary Anion Exchange Tests on Blyvooruitzicht Pregnant Solutions" T.V. Arden, R.S. Olson, J.J. Brunner & R.D. McDonald.