CEMENTITIOUS PROPERTIES OF METALLURGICAL SLAGS

A dissertation presented to the Faculty of Engineering,

University of the Witwatersrand

in fulfilment of the requirements for the Degree

of

MASTER OF SCIENCE IN ENGINEERING

by

Robert Dorsey Coale, Met. E.

1971

This work was carried out in the Department of Metallurgy,

University of the Witwatersrand

under the supervision of

Dr. P. R. Jochens, MSc. (Eng) (Rand), PhD

and

Mr. C. W. Wolhuter, BSc. (Eng) (Stell)

U N D E R T A K I N G

I hereby certify that this is my own work, and that it has not been submitted for a Master of Science Degree at any other University.

RD Coale

R. D. Coale

ACKNOWLEDGMENTS

The author wishes to record his appreciation of the assistance given to him by his supervisors, Dr. P. R. Jochens and Mr. C. W. Wolhuter.

SYNOPSIS

An investigation was made into the cementitious properties of metallurgical slags which fall in the four-component system SiO_2-Al_2O_3-MgO-CaO, notably those slags from the iron blast furnace. A series of slags have been chosen based on the following criteria:

SiO_2	:	20 - 50 Per cent
Al_2O_3	:	10 - 35 Per cent
MgO	:	0 - 35 Per cent
CaO	:	10 - 50 Per cent

Liquidus temperature less than 1600°C.

These criteria result in 101 slags which best reflect the slags available for the manufacture of cement.

The slags were prepared by melting the pure oxide components and quenching them into water. The quenched slags were ground and subjected to various tests:

1. True liquidus temperature determination
2. Primary Phase determination
3. Rate of quenching required to prevent crystallization.

Small test cylinders were made by mixing the ground slag with sand and $Ca(OH)_2$ activator and moulding the mixture. These were tested at various intervals (7, 14, 28, and 56 days) to determine their compressional strength.

Iso-strength curves, relating compressional strength to composition, were drawn on pseudo-ternary diagrams at constant Al_2O_3 levels. These provide a means for rapidly assessing the hydraulic strength of a slag based on composition.

Two statistical approaches, a correlation matrix and a multiple linear regression analysis, were made to determine if a linear relation-

ship between strength and composition exists. No such relationship was found.

The total combined water of hydration was determined for selected samples to determine if a relationship between strength and hydraulic reactivity existed. These results were inconclusive.

CONTENTS

CONTENTS (Continued)

I. GENERAL CONSIDERATIONS

1.1 Introduction

As world production of metals increases, so does production of associated metallurgical slags. Although new processes and technology have reduced the quantity of slag per unit of metal produced, increased demands for metals have increased the total amount of slag formed.

Although slags are formed during a number of pyrometallurgical processes, the major proportion of slag is derived from the iron and steel industry and ferro-alloy production. Slags themselves, if free from metal values, have little further use metallurgically, except when used as a fluxing material. Hence large quantities of slags must be disposed of by various metal producers. Several different industries have found slags to be a useful raw material for various applications.

Perhaps the most common use of raw, unprocessed slags is as aggregate, either as a concrete filler or as roadway and railway foundation material. Other uses of slags include slag ceramics which are produced by a process of controlled devitrification, slag wool for use as insulation material, foamed slag for use as a light-weight aggregate, and, depending upon their composition, as fertilizers. Slags are also frequently used for the manufacture of cement or as an addition to portland cement constituents. The subject of this thesis is the use of slags as cement.

1.2 Slag Cement

Blast furnace slag has been used as a raw material for the manufacture of cement for about 100 years [1]. These slags, which fall into the quaternary system SiO_2-Al_2O_3-MgO-CaO may vary greatly in their hydraulic properties depending upon their chemical composition, the presence of constituents other than those in the quaternary system, the amount of crystalline material in the quenched slag, and other considerations.

Blast furnace slag can be utilized as a cement with the addition of an activator, or, more commonly, as an addition to portland cement in varying proportions. Slag additions to portland cement can either be made to the cement clinker prior to grinding or as an addition to the mortar mix. The former results in an unequal particle size distribution between the cement and the slag, as the softer clinker will be preferentially ground. Addition of the slag to the mortar mix necessitates separate grinding of the two constituents.

Mixtures of portland cement and blast furnace slags fall generally into three categories depending upon the weight ratio of the two constituents [2].

Specification	Per Cent Blast Furnace Slag
Blast furnace cement 35	<35
Blast furnace cement 35/80	35 - 80
Ciment de laitier au Portland	>85

Unassociated MgO (periclase) in portland cement clinkers has been shown to be deleterious to the cement because of the volume increase experienced when this constituent hydrates to form brucite [3]. Since expansion may occur a considerable length of time after the cement has set, thus disrupting the entire matrix, the amount of periclase allowed in cement clinker is regulated by various specifications, generally to less than five per cent. This specification has also been applied to blast furnace slag cements, although various workers [3,4,5,6] have shown that when maintained in the glassy state the MgO in blast furnace slags is not harmful.

The risk of lime unsoundness has also led to certain restrictions being imposed on the CaO content of blast furnace slag cements. Lime unsoundness results from the phase change beta to gamma dicalcium silicate ($2CaO.SiC_2$) and is accompanied by a volume increase of the slag.

Several workers have proposed composition specifications of the slag which will prevent "falling" because of lime unsoundness [7,8,9], and it has been shown that rapid quenching of a blast furnace slag prevents the crystallization of dicalcium silicate and thus precludes the possibility of the phase change.

1.3 Assessment of the Hydraulic Properties of Slags

Some investigations have been made into the suitability of high-magnesia or high-lime slags for cement production [3,4,6], however the entire range of slag compositions available for cement manufacture has not been studied to determine the extent of those slags suitable for cement.

Various composition formulae have been proposed for the assessment of a slag based on its composition. Of these, the modulus

$$\frac{CaO + MgO + {}^{1}/{}_{3}\,Al_2O_3}{SiO_2 + {}^{2}/{}_{3}\,Al_2O_3} \geq 1$$

has been one of the most popular [5].

Other related formulae include $\frac{CaO + MgO + Al_2O_3}{SiO_2} \geq 1$, $\frac{CaO}{SiO_2} \geq 1.2$, and $\frac{CaO + Al_2O_3 + CaS + MgO}{SiO_2 + MnO} \geq 1.5$. These formulae are based on experience and have been used to indicate the hydraulic value of a slag. The validity of these formulae over a wide compositional range has not been established.

One of the most important criteria for assessing slags for use as cement is that they do not contain more than about 15 per cent crystalline material. Not only might crystalline material lead to unsoundness as discussed above, but crystalline slag possesses little or no hydraulic properties [10]. For this reason, slags which cannot be successfully quenched to yield a glassy product will be unsuitable for cement manufacture. Therefore, a determination of the quenching characteristics is necessary.

Parker and Nurse [11] have combined both a composition modulus and the percentage glass into a strength index:

$$I = 0.38G\,(M - 0.78) + 75.0$$

where

I = Strength index of a 65/35 portland cement/slag mixture

G = Per cent glass

$$M = \frac{CaO + MgO + 1/3Al_2O_3}{SiO_2 + 2/3Al_2O_3}.$$

It is therefore proposed to examine a number of slags with respect to not only their hydraulic capabilities but also to their overall suitability as cement.

1.4 Metallurgical Slags

Slags which might be considered for use as cement come from three main sources:

a. iron blast furnace

b. steelmaking processes

c. ferro-alloy production.

All of these slags fall basically into the quaternary system SiO_2-Al_2O_3-CaO-MgO but contain varying amounts of other material. In addition to those slags listed above, non-ferrous slags may also fall generally into this quaternary system, but these slags usually contain significant amounts (more than 10 per cent) of material not falling into the SiO_2-Al_2O_3-MgO-CaO system, which would probably affect the granulation behaviour and the cementitious properties of the slag.

Table I is a tabulation of the analyses of several types of metallurgical slags which have a composition suited to warrant their application as a constituent of cement.