CHAPTER 8

CHROMIUM(III) AS A REDUCING AGENT FOR THE REMOVAL OF MANGANESE OXIDES FROM FOSSIL BONES

Chromium can reduce manganese oxides in the environment by the following reaction:

$$3MnO_2(s) + 2Cr^{3+} + 12H^+ \rightarrow 3Mn^{2+}(aq) + 2Cr^{6+}(aq) + 6H_2O(l) \qquad 8.1$$

8.1 Procedure

All solutions of different concentrations were made from a stock solution and fresh solutions were prepared each day. The fossil bones were placed into the respective solutions and left for the stipulated time periods. Other conditions controlled during experimentation were pH and concentration of Cr(III).

8.2 Optimization

The optimization procedure for the use of Cr(III) as a method of removing manganese oxide coatings from fossil bones was carried out using random test points performed in duplicate comprising different pH and concentration values. This was done to determine the validility and potential practical use of this method with respect to implementation on a large scale. Once extreme test parameters were used and evaluated, it was established that the kinetics were extremely slow. Some mechanical assistance is also required after the coated fossil fragment is soaked in the Cr(III) solution, which is not desirable as damage could be incurred to the fossil specimen. This method was also found to

discolour the specimen, turning the surface green, which is also evidence that the Cr(III) is strongly bound to the bone surface.

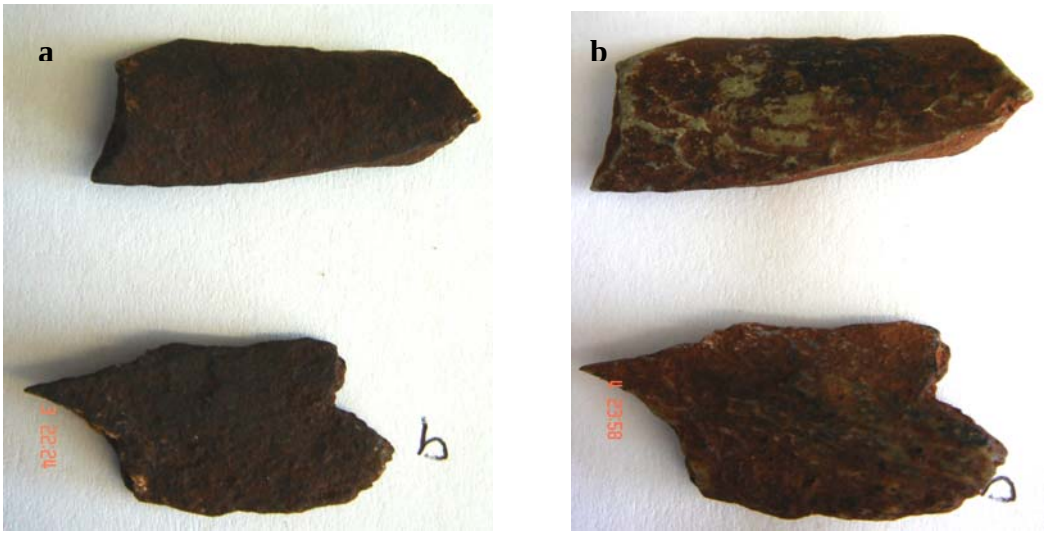

Figure 8.1 Manganese oxide coated fossil bone fragments **a,** before treatment; **b** After treatment in a 0.01 mol L^{-1} Cr(III) solution at natural pH and gentle sponging.

Figure 8.2 Manganese oxide coated fossil bone fragments **a** and **b,** after soaking in a 0.01 mol L^{-1} Cr(III) solution with repeated sponging of the fossil specimen.

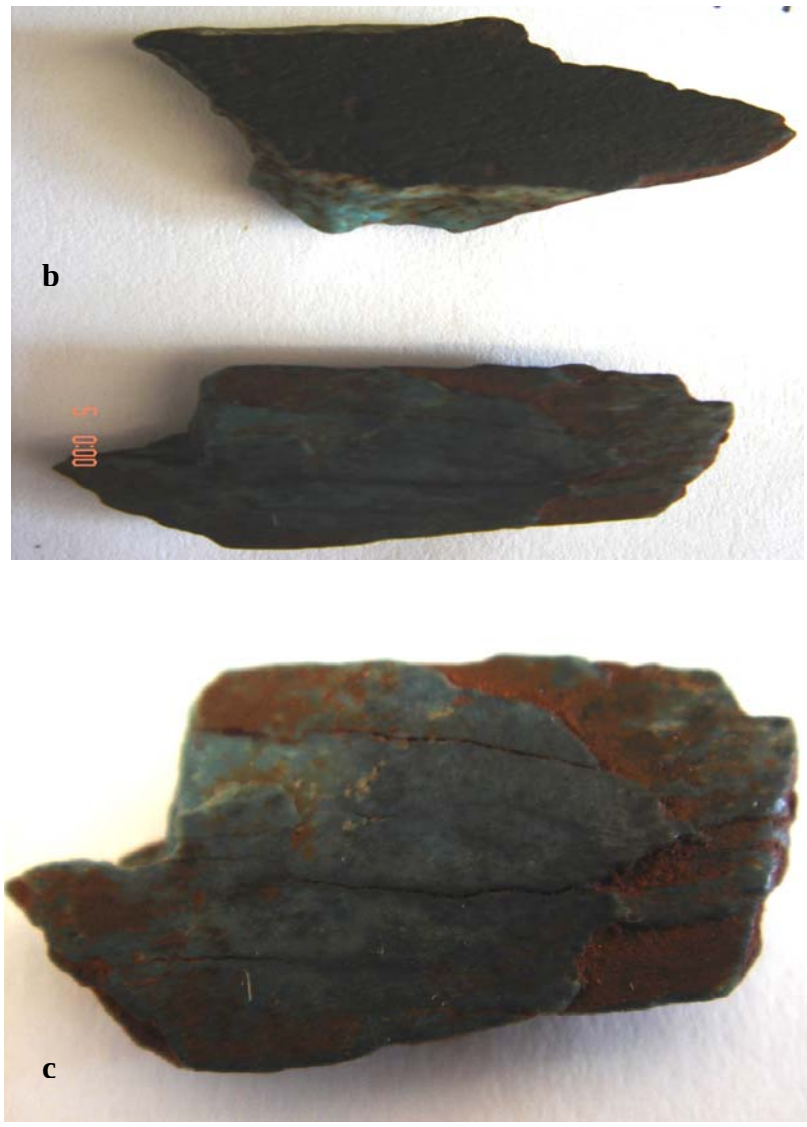

Figure 8.3 Manganese oxide coated fossil bone fragment **a,** before treatment in a 0.1 mol L^{-1} Cr(III) solution at natural pH. **b,** two duplicate specimens after soaking in a 0.1 mol L^{-1} Cr(III) solution and gentle sponging; **c,** higher magnification showing the green surface of an individual bone fragment after treatment in 0.1 mol L^{-1} solution.

Although the Cr(III) concentrations used were ten times different in magnitude, the overall appearance and removal of the fossil bone coating appears to be similar for both specimen samples. This method appears to cause green staining of the bone surface

which could mask the degree of manganese oxide removal. The green appearance of the bone is due to the adsorption of Cr(III) onto the surface and penetration into the matrix.

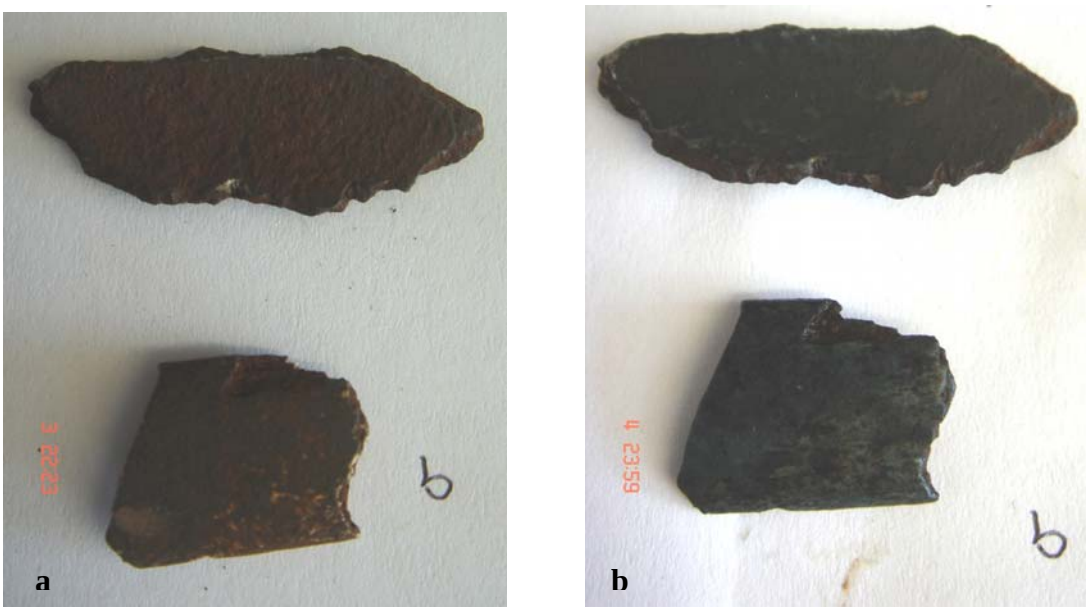

Figure 8.4 Manganese oxide coated fossil bone fragments **a,** before treatment; **b,** bone fragments after treatment in a 0.2 mol L^{-1} Cr(III) solution.

b

Figure 8.5 Visible glossy green surface colour in **a** and **b** caused by the 0.2 mol L^{-1} solution after removal of most of the manganese oxide surface coating with sponging used to aid the efficiency of the process.

The optimization was performed using three different concentrations all at their natural pH values. These pH values differed sufficiently from each other to have a direct influence on the redox chemistry of the solution/solid interface. It is difficult to establish the degree of coating removal from bone to bone as this method discolours the bone, leaving a dark green Cr(III) tint. From other redox studies carried out on the reduction of manganese oxides using Cr(III), it is evident that a number of factors can influence the rate and efficiency of manganese oxide reduction (Eary and Rai, 1987; Fendorf and Zasoski, 1992; Apte *et al*., 2005; Apte *et al*., 2006). This becomes evident in the optimization experiments that were performed. From the figures above it can be observed that there is no clear relationship between pH and the concentration of Cr(III) used in this investigation method. Other factors also influence the oxidation reaction, such as surface charge, re-adsorption of the oxidation product, Cr(VI) to the bone surface, thus

preventing Cr(III) interaction with the manganese oxide surface, and other transport factors (Fendorf and Zasoski, 1992).

8.2.1 Cr(III) concentration and pH

The change in pH of different concentrations of Cr(III) in which different manganese oxide coated fossil bones were soaked were measured. This was done in order to try and establish whether the Cr(III) concentration or the initial pH of the treatment solution has the most influential effect on the reduction of the manganese oxide coating on the surface of the fossil bone specimen.

Table 8.1 Change in pH of Cr(III) solution containing manganese oxide coated fossil bone fragments soaked in three different concentrations of Cr(III) performed in duplicate.

Cr(III) Concentration/ mol L^{-1}	**Initial pH**	**Final pH**
0.01 a	3.06	3.46
b	3.10	3.42
0.1 a	2.57	2.79
b	2.63	2.93
0.2a	2.22	2.49
b	2.23	2.62

Table 8.2 Change in pH of 0.01 mol L^{-1} Cr(III) solutions at fixed initial pH values containing three different manganese oxide coated fossil bone fragments performed in duplicate.

Sample	Initial pH	Final pH
a	3.04	3.51
b		3.50
a	4.05	3.95
b		4.00
a	5.10	4.26
b		4.09

Table 8.3 Change in pH of 0.1 mol L^{-1} Cr(III) solutions at fixed initial pH values of Cr(III) solutions containing three different manganese oxide fossil bone fragments performed in duplicate.

Sample	Initial pH	Final pH
a	3.00	2.91
b		2.90
a	4.00	3.05
b		3.03
a	4.74	3.27
b		3.14

The overall trend observed in tables 8.1, 8.2 and 8.3 above is a decrease in pH as the manganese oxide coated fossil specimen is soaked in the Cr(III) solution. As the initial pH of the solution was increased, the difference between the initial and final pH values increases negatively. For the 0.01 mol L^{-1} Cr(III) concentration there was an increase in pH with time for the initial pH of 3.04, however for the 0.1 mol L^{-1} Cr(III) solution the change in pH for the initial pH of 3.0 was negative, indicating that the Cr(III) concentration causes a shift in the pH value's change as the reaction proceeds.

A possible cause, although not observed here could be due to a changing reaction stoichiometry with solution composition resulting in the formation of MnOOH(s) as the reduction product of ß-MnO_2(s) at the higher pH and Cr(III) concentration as opposed to Mn^{2+} as shown (8.2) below (Eary and Rai, 1987):

$$CrOH^{2+} + 3ß\text{-}MnO_2(s) + 3H_2O \rightarrow HCrO_4^{-} + 3MnOOH(s) + 3H^{+} \qquad 8.2$$

This could result in the observed decrease in pH as the initial pH value and Cr(III) concentration is increased. It should also be noted that there are many processes occurring at the surface and in solution, thus these combined processes of Cr(III) oxidation, Cr(VI) adsorption, manganese redox speciation (Mn(IV) and/or Mn(III) oxide composition and ß-MnO_2(s) acidic dissolution, make the understanding and determination of certain stoichiometry, trend prediction and other reaction kinetic parameters complex (Eary and Rai, 1987).

8.2.2 Kinetics investigation for Cr(III) reduction of manganese oxides on fossil bone fragments

The role and trend for different Cr(III) concentrations of the treatment solution was investigated. The rate of manganese evolution was measured over a wide range of Cr(III) concentrations at different initial pH values.

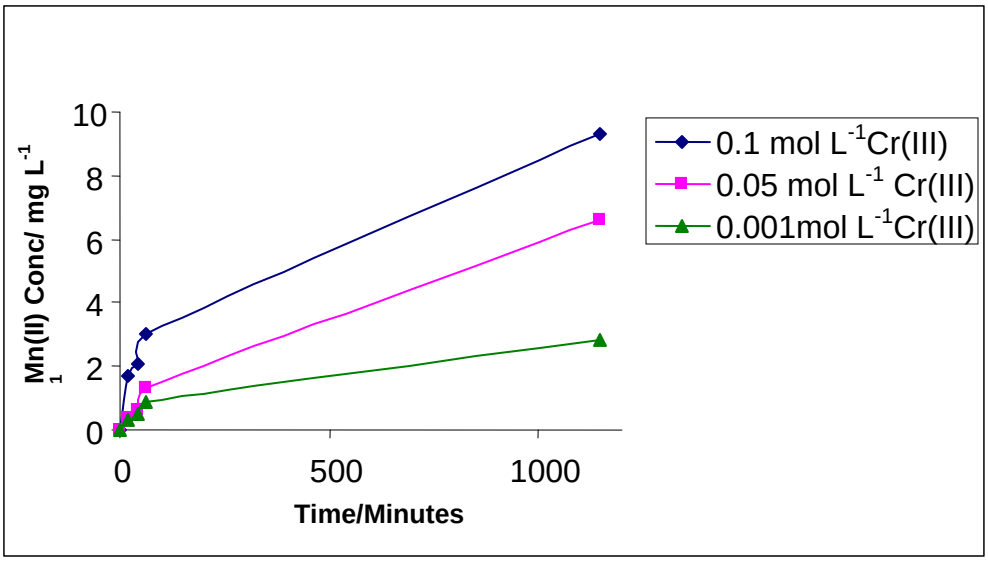

Figure 8.6 Mn(II) evolution trends as a function of time for six different manganese oxide coated fossil bone fragments placed in three Cr(III) solutions, at initial pH of 3.04, 4.05 and 5.10 performed in duplicate. Cr(III) concentrations used 0.001 mol L^{-1}, 0.05 mol L^{-1} and 0.1 mol L^{-1}

A manganese oxide coated bone fragment was broken into three approximately equal pieces. Each fragment was placed in a different concentration of Cr(III) and the rate of Mn(III) evolution was determined. The rate increased with increasing Cr(III) concentration. This was done to demonstrate that the reduction method is dependant upon

the concentration of the Cr(III) solution. This does not, however, explain the trends obtained for the qualitative or visual optimization of manganese oxide removal from the three fossil fragments. It can thus be observed that other factors as mentioned above can negate the effect of Cr(III), and prevent efficient surface electron transfer, and thus slow the kinetics of this cleaning method for these fossil bones (Eary and Rai, 1987; Fendorf and Zasoski, 1992; Apte, *et al*., 2005; Apte, *et al*., 2006).