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SELECTIVE REMOVAL OF CHROMIUM FROM SULPHURIC ACID LEACH LIQUOR OF ILMENITE ORE BY SOLVENT EXTRACTION WITH TRIOCTYLAMINE

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ABSTRACT. The selective removal of chromium, a trace impurity that degrades the whiteness of titanium(IV) oxide pigments, from sulphuric acid leach liquor of ilmenite, was investigated by solvent extraction with xylene solutions of trioctylamine. Important factors of commercial significance affecting the extraction operation have been examined. More than 99% of the chromium was selectively removed in multiple batch extractions from the leach liquor and titanium losses were minimal (< 1%). The chromium content of extracted solutions was reduced to less than 1 ppm and thermal hydrolysis of these solutions yielded white titanium(IV) oxide pigments that are suitable for use in the coatings pigment industry.

INTRODUCTION

To date, titanium(IV) oxide pigments for the paint, paper, and plastic industries in Nigeria are still being imported from overseas countries. However, there has been an increasing demand for local source of pigments over the last one decade. This is due to high cost of importation, which makes the use of imported pigments less economical, particularly for small scale establishments.

For the past eight years, Olanipekun and co-workers [1-7] have been investigating a suitable manufacturing process of white titanium(IV) oxide pigment, using a local ilmenite ore as the raw material. In this regard, several papers [1-7] have been published concerning the leaching reaction of the ilmenite ore in various mineral acids. Unfortunately, titanium(IV) oxide pigments prepared from the Nigerian ilmenite ore usually are not pure white and as such could not be utilized in the coatings pigment industry.

Among the trace impurities, chromium has been indicated to have the most adverse effect on whiteness and photochemical properties of titanium(IV) oxide pigments. Many other impurities, including iron, are reduced during normal processing to low concentrations where they do not affect whiteness [8-10].

The elimination of chromium from titanium(IV) oxide pigments is a strategic problem. Many studies have indicated the efficacy of a solvent extraction process in the removal of chromium from different acid media. Among the several organic reagents reported, amine extractants were particularly found [11] to exhibit high selectivity for chromium in the presence of high concentrations of titanium and iron in ilmenite ore solutions. In a recent study [12], the extraction of chromium(VI) from sulphuric acid medium with primary amines was investigated by the distribution method and infrared spectroscopy. There has also been a report [13] on the extraction of chromium(VI) by a column chromatographic technique using polytetrafluoroethylene as the support, tributyl phosphate as the stationary phase and 0.8 M hydrochloric acid as the mobile phase. So far, no attempt has been made to remove chromium from leach liquors of Nigerian ilmenite ore.

This paper deals with selective removal of chromium from sulphuric acid leach liquor o Nigerian ilmenite ore by solvent extraction with xylene solutions of trioctylamine (TOA under practical conditions in which the concentrations of titanium and iron in the leach liquo are sufficiently high. Trioctylamine was chosen as the extractant for chromium because it i immiscible with water, and is readily and commercially available; moreover, it would no reduce chromium(VI).

Equation (1) shows the chemical reaction between TOA and chromium, where R i $[(CH_2)_7CH_3]_3$

$$2[(R_4N)^+(HSO_4)^-]_{org} + [Cr_2O_7^{2-}]_{aq} \rightleftharpoons [(R_4N)_2^{2+}(Cr_2O_7)^{2-}]_{org} + 2[HSO_4^-]_{aq} \quad (1)$$

It can be observed from equation (1) that the $[H^+]$ should have no drastic effect o chromium(VI) extraction and that cationic species should not be extracted. At high aci concentrations, however, the chromium(VI) anion must compete with the anion of the aci and a decrease in chromium extraction would be expected.

The present work was carried out as a continuation of a recent study [3] on the leaching o a Nigerian ilmenite ore in concentrated sulphuric acid solutions, the first step in the industria production of titanium(IV) oxide pigments by the "sulphate" process.

In the production of titanium(IV) oxide pigment by the "sulphate" process, ilmenite i dissolved in sulphuric acid and chromium is present in this solution as chromium(III) Extraction of chromium from this solution with amines is apparently practicable only after i has been oxidized to extractable anionic chromium(VI) species [11, 12]. Chromium(III) ma be oxidized in acid solutions by various compounds such as persulphates, chlorates, lead(II oxide, ceric salts, permanganate, or electrolytically at a PbO anode. However, sodium chlorat has been found [11] to be the most effective Cr(III) oxidizer and hence it is selected for use i this study.

EXPERIMENTAL

Reagents. All reagents were of analytical grade. Sulphuric acid leach liquor was prepared b digestion of 100 μm fraction of an ilmenite ore (10 g) from the Jos Plateau, Nigeria with 95 H_2SO_4 (50 mL) at 170 °C for 2 h. The reaction product was dissolved in water at 60 °C, the allowed to cool, and the insoluble residue was filtered off. The filtrate was diluted wit distilled water to mark in a 500 mL volumetric flask [7]. The diluted solution was analyze for Ti, Fe(II), Cr(III), V(IV), and free H_2SO_4 using standard chemical analysis procedure [14]. TOA solutions of different concentrations were prepared in xylenes and precondition by mixing with 3 M H_2SO_4 containing a known amount of $K_2Cr_2O_7$, allowing the organic an aqueous phases to separate, then stripping the chromium from the organic phase by shakin with 1 M Na_2CO_3. This treatment was repeated until the Cr(VI) reducing impurities we removed, as indicated by little or no formation of green coloured Cr(III) species on recontac with fresh acidic Cr(VI) solution [11].

Oxidation of chromium(III) in ilmenite leach liquors. A given volume (100 mL) of th sulphuric acid leach liquor containing known amounts of chromium(III), vanadium(IV) an iron(II) was placed in a round-bottomed flask fitted with a heating mantle, reflux condense mechanical stirrer, and thermometer. The quantity of sodium chlorate required to oxidiz chromium(III) along with vanadium(IV) and iron(II) was calculated from stoichiometry. Th effects of quantity of $NaClO_3$ used, ore solution concentration, temperature, and heating time on the oxidation of Cr(III) in ore solution was determined. The ore solution was concentrated at reduced pressure when required, $NaClO_3$ was added, and the solution was heated at a specific temperature for a fixed period of time [11].

Extraction of chromium from oxidized ilmenite ore solutions. Equal volumes (25 mL) of ilmenite ore solution and TOA solution were placed in a separatory funnel. The contents were vigorously shaken for 2 to 3 min at 25 °C and left to settle until the phases separated clearly. The aqueous phase was analyzed for chromium, iron, and vanadium by flame atomic absorption spectrophotometry, using air/acetylene flame for both Cr and Fe, and nitrous oxide/acetylene for vanadium, and for titanium by colorimetry [14]. The percentage extractions and distribution ratios of chromium were calculated from its concentrations in the aqueous phase before and after the extraction [15].

RESULTS AND DISCUSSION

The percentage of chromium oxidized as a function of heating time and quantity of sodium chlorate added to ore solution is shown in Figure 1. Chromium oxidation is obviously enhanced by an increase in quantity of $NaClO_3$ added to solution. In order to ensure complete oxidation of chromium(III) in ore solution, it seems economically reasonable to use between two to three times the calculated $NaClO_3$ requirement for a heating period of 30 to 40 min at 100 °C.Figure 2 shows the effect of ore solution concentration on chromium(III) oxidation. The oxidation efficiency increases with increasing ore solution concentration. In a study on the dissolution of ilmenite in sulphuric acid [16], it was observed that titanium ions are readily hydrolyzed in dilute acid solutions and precipitated as titanium(IV) oxide which hinders further acid attack. However, such a precipitation was not encountered when ilmenite was leached with concentrated sulphuric acid solution [3]. Hence, the observed increase in oxidation efficiency with increasing ore solution concentration was perhaps due to the stability of ore solution towards thermal hydrolysis.The effect of temperature on oxidation of chromium(III) is presented in Figure 3. The percentage of chromium oxidized also increases rapidly as the temperature approaches 100 °C due to the vigorous nature of reaction at high temperatures.

Table 1 shows the effect of ore solution concentration on extraction of chromium. The percent chromium extracted increases as the solution is diluted. This observation is not unexpected for the fact that chromium concentration normally should decrease as the ore solution is diluted. Since TOA concentration remains constant, more of it would be available for the complexing of chromium, which is present at lower concentrations in dilute ore solutions. In other words, there appears to be an inverse relationship between the percentage of chromium extracted and the chromium concentration in the ore solution at constant TOA concentration; the lower the concentration of chromium in ore solution, the higher are the percentage extraction and distribution ratio of chromium. However, a lower limit of 75 g TiO_2/L is set by the instability of solutions towards hydrolysis. Oxidized ore solutions containing 100 g TiO_2/L were stable for months without precipitation of solids. Even at an ore solution concentration as high as 200 g TiO_2/L, the distribution ratio of 3.0 indicates favourable chromium extraction. In all cases, chromium was found to be the only metal extracted; besides, titanium losses were always less than 1 %.

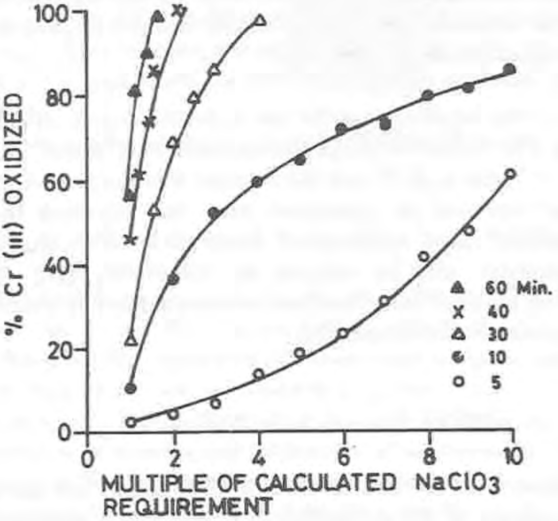

Figure 1. Effect of heating time and amount of sodium chlorate on oxidation of chromiu
(250 g TiO$_2$/L, 100 °C).

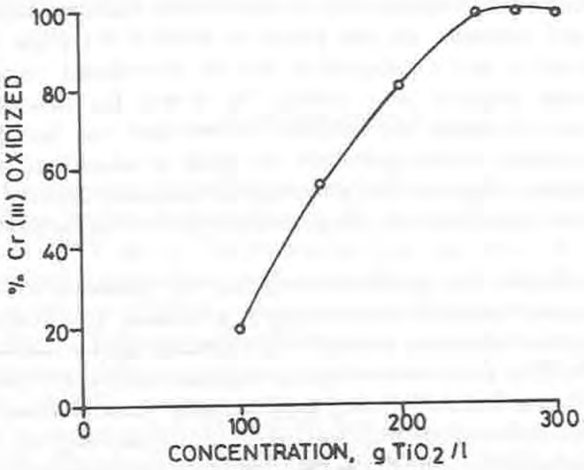

Figure 2. Effect of ilmenite ore solution concentration on oxidation of chromium (100 °C,
min, three times calculated NaClO$_3$ requirement).

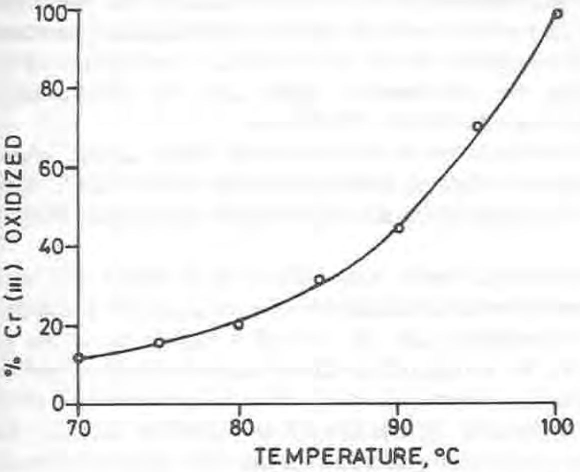

Figure 3. Effect of temperature on oxidation of chromium (250 g TiO_2/L, 40 min, three times calculated $NaClO_3$ requirement).

Table 1. Effect of ore solution concentration on extraction of chromium.

Before extraction[a] TiO_2, g/L	Cr, mg/L	Cr in aq phase after extraction[b], mg/L	% Cr extracted	Distribution ratio
200	152	38	75.0	3.0
175	130	27	79.2	3.8
150	116	17.5	84.9	5.6
100	96.3	9.6	90.0	9.0
75	61.2	4.5	92.6	12.6

[a] Ilmenite ore solution (250 g TiO_2/L) oxidized with four times calculated $NaClO_3$ requirement at 100 °C for 30 min, then diluted as indicated. [b] One extraction, aq/org volume ratio = 1:1, with 6 (v/v) % trioctylamine in xylene.

Table 2. Effect of trioctylamine (TOA) concentration on extraction of chromium.

TOA concentration (v/v) % in xylene	Cr in aq Phase after extraction[a], mg/L	% Cr extracted
2	46.4	51.8
4	23.8	75.3
6	9.6	90.0
8	8.2	91.5
10	7.0	92.7

[a] Ilmenite ore solution (250 g TiO_2/L) oxidized with four times calculated $NaClO_3$ requirement at 100 °C for 30 min, then diluted to about 100 g TiO_2/L; one extraction, aq/org volume ratio = 1:1.

The influence of TOA concentration on chromium extraction can be derived from Table The amount of chromium removed increases as TOA concentration is increased. However seems economically advantageous to use TOA solutions of concentration of 6 (v/v) % xylene since increasing the concentration further did not significantly influence percentage of chromium extracted.

Table 3 shows the amount of chromium extracted at various aq/org volume ratios. Sin extractions of oxidized ore solutions containing about 100 g TiO_2/L indicate increas chromium extraction as the ratio decreases and reaches a maximum (>99.8 %) at an aq/ volume ratio of 1:2.

The effect of multiple batch extraction on removal of chromium is presented in Table The percentage of chromium removed increases with each successive extraction. Not less th 99.7 % of chromium was removed after six successive extractions, aq/org volume ratio each extraction being 5/1; the chromium content of extracted solutions was less than 1 pp Thermal hydrolysis of some extracted solutions yielded white titanium(IV) oxide pigmen In an earlier study carried out by Olanipekun [7], the pigments prepared from unextract sulphuric acid leach liquors of the Nigerian ilmenite ore were light brown in colour.

Table 3. Effect of aqueous/organic volume ratio on extraction of chromium.

Aq/org Volume ratio	Cr in aq phase after extraction[a], mg/L	% Cr extracted
5:1	52.4	45.6
3:1	36.2	62.4
1:1	9.6	90.0
1:1.5	0.8	99.2
1:2	<0.1	>99.8

[a] One extraction with 6 (v/v) % trioctylamine in xylene. Other conditions are as in footnote of Table 2.

Table 4. Effect of multiple batch extraction on removal of chromium.

No. of extraction	Cr in aq phase after extraction[a], mg/L	% Cr extracted
1	52.4	45.6
2	39.2	59.3
3	14.4	85.0
4	6.5	93.2
5	0.6	99.4
6	<0.1	>99.8

[a] Extraction with 6 (v/v) % trioctylamine in xylene; aq/org volume ratio = 5:1. Other conditions are as footnote of Table 2.

In conclusion, this study has clearly shown the efficacy of TOA-xylene extractant selective removal of chromium from sulphuric acid leach liquors of the Nigerian ilmenite o White titanium(IV) oxide pigments prepared from extracted solutions are of good quali suitable for use in coatings pigment industry in Nigeria which still depends on import pigments for use. Work is in progress on the stripping of chromium from the organic pha

Furthermore, cost analysis together with scale-up experiments for the proposed procedure would constitute part of future investigations.

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