The Effect of Oxidation on the Flotation of Chromite and Associated Minerals

UNITED STATES DEPARTMENT OF THE INTERIOR
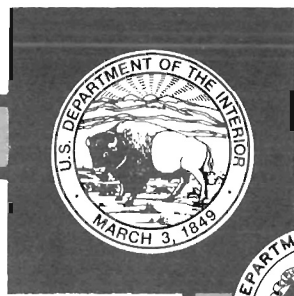
UNITED STATES BUREAU OF MINES

U.S. Department of the Interior
Mission Statement

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Cover: Flotation testing at Salt Lake City Research Center.

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By D. G. Kotlyar, W. K. Tolley, and D. A. Rice

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THE EFFECT OF OXIDATION ON THE FLOTATION OF CHROMITE AND ASSOCIATED MINERALS

By D. G. Kotlyar,[1] W. K. Tolley,[2] and D. A. Rice[3]

ABSTRACT

The effects of oxidation on the flotation of chromite and olivine were studied in an effort to improve chromite recovery from domestic sources. The flotation behavior of pure chromite, pure olivine, and a chromite gravity concentrate were investigated. Minerals were heated in air at 50 °C for 3 h, or at 150 or 250 °C for 18 or 70 h to oxidize the mineral surfaces. The flotation response for the oxidized minerals was measured as a function of collector concentration and pH. Redox potential in the flotation slurries was measured. Freshly prepared chromite floated well between pH 2.2 and pH 4.5 but poorly at greater than pH 5. Oxidation at 150 °C increased chromite floatability above pH 5 to about 30%. In contrast, oxidation did not measurably affect olivine flotation. This suggested that controlled oxidation may improve selectivity in the flotation of chromite from olivine. This concept was tested using a chromite gravity concentrate. Both flotation recovery and chromium oxide grade increased slightly following oxidation of the concentrate. Although the benefit from oxidation was small, this result shows promise for improving flotation selectivity using oxidation.

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INTRODUCTION

Chromium and its source mineral chromite are used extensively in stainless steels, high-temperature alloys, chemicals, and high-quality refractories. Significant chromite deposits are found in southwest Oregon and in the Stillwater Complex near Nye, MT. However, chromite is not produced domestically for several reasons. Domestic chromite deposits are relatively small and most are of a lower grade than other resources throughout the world (*1*).[4] Most domestic chromite ores also contain silicate gangue minerals that are difficult to remove. Currently, all chromite used in the United States is imported (*2*). Typical grades of chromite concentrates used in industry contain 40% to 50% chromium oxide (Cr_2O_3) and have chromium-to-iron ratio of 1.5:1 to 3:1.

The U.S. Bureau of Mines (USBM) showed that chromite can be selectively concentrated from some low-grade resources by flotation using an amine collector (*3-4*). However, amine flotation is ineffective when the ore contains olivine as the primary gangue mineral (*4*). As a result, the technology to treat many domestic chromite ores is lacking.

The possibility of improving chromite beneficiation was indicated by data in the literature. Smith (*5*) found that oxidizing a domestic chromite at 50 °C for 3 h improved its flotation in the range pH 4 to pH 12 using 1×10^{-4} molar concentration (*M*) sodium dodecylsulfate (SDS) solution. These data are plotted in figure 1. Smith reports flotation results for fresh silicate minerals, but flotation of the similarly oxidized minerals is not reported. However, these data suggest that oxidation and redox control in

Figure 1
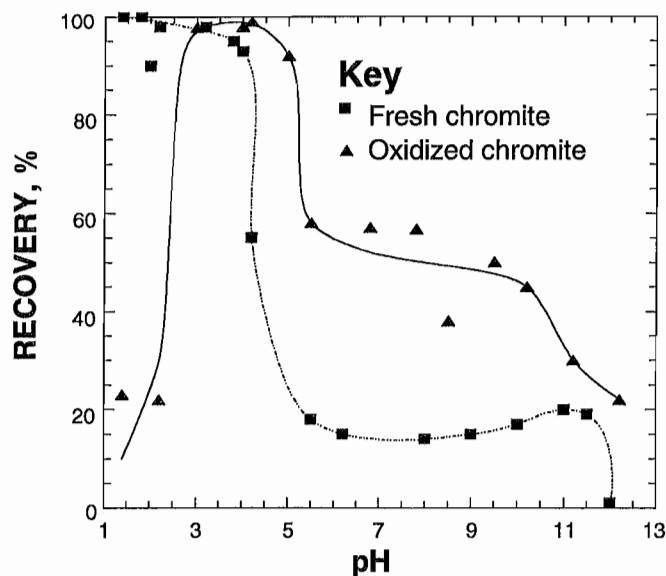
Chromite flotation in SDS showing the effect of oxidation to improve flotation in the range pH 6 to pH 8.

flotation may prove to be significant in enhancing chromite floatability.

Little information is available on the effects of oxidation on the flotation of chromite and associated gangue minerals. The USBM initiated research to collect fundamental data on oxidation in chromite flotation and to use this information to improve beneficiation technology.

EXPERIMENT MATERIALS

Pure, monosized chromite was obtained from American Colloid Co. This material is used as refractory sand. X-ray diffraction (XRD) analyses of the sample confirmed chromite as the predominant phase. Examination under the scanning electron microscope (SEM) showed that the sample contained approximately 97% chromite.

Pure, monosized olivine was obtained from Applied Industrial Material Corp. This material also is used as refractory sand. XRD analyses identified magnesium-iron silicate [$(Mg,Fe)_2SiO_4$]. SEM examination found that the sample contained approximately 85% olivine, with impurities of iron-magnesium-calcium silicates and chromite.

A sample of chromite ore was obtained from the deposit at Mouat Mountain near Nye, MT. Chromite was beneficiated by gravity concentration and electrostatic

separation. This concentrate contained approximately 45% to 55% chromite, 40% to 50% olivine, and 5% to 10% calcium, magnesium, and iron silicates. SEM examination of the sample show that the minerals were liberated. Chemical analyses of all three materials are shown in table 1.

Table 1.—Chemical analyses of materials, weight percent

	Chromite	Olivine	Chromite Ore
Cr_2O_3	48	NAp	20
Fe	23	6	15
SiO_2	0.6	42	21
MgO	10	48	27
Al_2O_3	13	0.2	4.7
CaO	2.8	2.8	1.2
Cr/Fe	1.4	NAp	1.3

NAp   Not applicable.

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[4]Italic numbers in parentheses refer to items in the list of references at the end of this report.

EXPERIMENT SAMPLE PREPARATION

Before the test work started, the test minerals were divided into 150-g samples using a rotary splitter. These individual samples were stored in closed plastic bags until used. All samples were dry ground in a ceramic ball mill as needed. Grinding times were adjusted to obtain similar size distributions for each material. The pure chromite and chromite concentrate were ground for 10 min; the pure olivine sample was ground for 30 min. Typical size distributions of the ground materials are plotted in figure 2.

Oxidized samples were prepared using freshly ground materials. The freshly ground samples were heated in air at 50 °C for 3 h, or at 150 or 250 °C for 18 or 70 h. These conditions were chosen to parallel Smith's test conditions (5). Several samples of freshly ground minerals were floated immediately after grinding as baseline tests.

EXPERIMENT FLOTATION PROCEDURE

Flotation tests were performed using a laboratory Denver flotation machine. The prepared mineral samples were poured into a 2.8-L flotation cell. The samples were deslimed twice by thoroughly suspending the solids in water, allowing the suspension to settle for 1 min, and decanting the supernatant liquid. Deionized water then was added to obtain a pulp density of 5.4% solids. The pH was adjusted using sulfuric acid or sodium hydroxide as required. Predetermined amounts of SDS, used as both collector and frother in the tests, were added and the slurry was conditioned for 2 min. The samples then were floated for 3 min using air as the flotation gas at a constant impeller speed of 1,100 rpm. Following flotation, the pH and redox potential (Eh) in the pulp were measured. Eh readings were taken using a gold electrode in combination with a silver chloride reference electrode. Potentials are reported relative to the standard hydrogen electrode.

Recoveries of the pure minerals were calculated using the weights of feed and concentrates. Grades and recoveries from the chromite concentrate were calculated based on wet-chemical analyses of the feed, floated product, and tail.

Figure 2
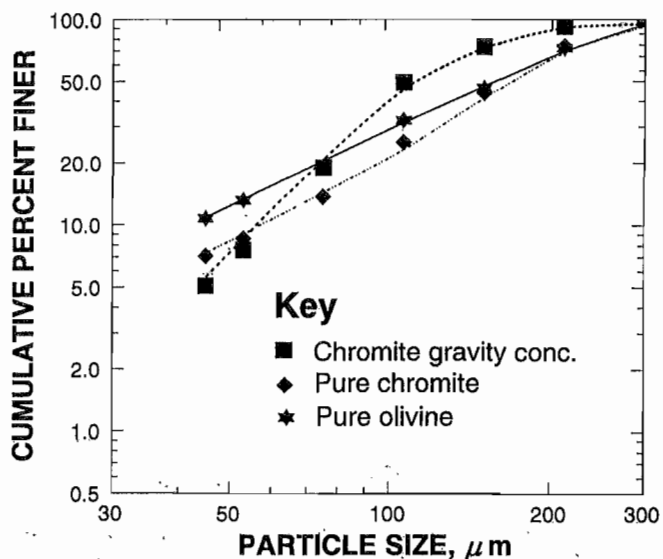
Particle-size distributions of pure chromite, pure olivine, and chromite gravity concentrate after grinding in ceramic mill.

Figure 3
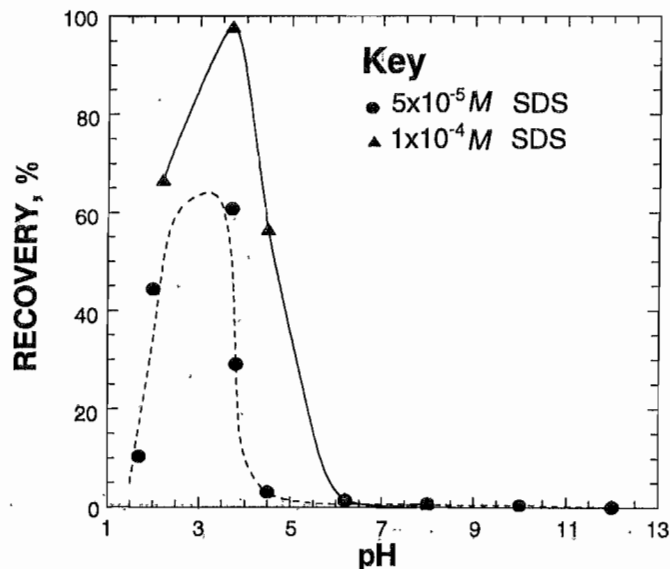
Flotation of freshly ground, pure chromite as a function of pH and SDS collector concentration showing poor recoveries above pH 6.

CHROMITE FLOTATION

The recovery curves plotted in figure 3 demonstrate that chromite recovery is highly dependent upon pH and SDS concentration. Freshly ground chromite floats well between pH 2 and pH 4.5. It floats extensively in $5\times10^{-5}M$ SDS; however, $1\times10^{-4}M$ SDS is needed for complete chromite recovery in this pH range using this particular material. Recovery is poor at pH 5 and virtually disappears above pH 6 regardless of SDS concentration.

Particle size also strongly affects floatability. Coarse chromite is more difficult to float with SDS than is fine chromite. Typical size distributions of chromite float and tail products are shown in figure 4. These data show that the float product is considerably finer than the tail. Chromite recovery could likely be increased by modifying the grinding step to obtain a better size distribution for flotation.

Figure 5 plots the recovery of chromite oxidized at 50 °C for 3 h. Recovery again depends strongly on pH and SDS concentration. The oxidation appears to have a slight effect on flotation of the pure chromite. Flotation is reduced at pH 4 and slightly improved at pH 6. However, Smith (5) observed that oxidation had a much stronger effect of increasing flotation between pH 6 and pH 10. Several differences in chemistry and procedure may account for the differences in flotation response:

1. These tests were performed with a Denver flotation machine using air as the flotation gas. Smith's tests were conducted in a Hallimond flotation cell using nitrogen as the flotation gas.

2. The chromite in the present study contains a higher amount of chromium than the chromite tested previously. Dallaire (6) found that chromite flotation with a sulfonate collector markedly decreased as chromium content in the mineral increased from 47% to 55%; thus, the chromite in the present study may be less amenable to flotation using an anionic collector.

3. The chromite in the present study had a coarser particle-size distribution. The chromite was ground to -300 μm for this study whereas Smith used the 105×149 μm fraction. Thus, the differences in flotation behavior could result from a combination of differences in test equipment, chromite composition, and particle size.

Since oxidation at 50 °C had only a small effect on flotation, more severe oxidation conditions were tested.

Freshly ground chromite was oxidized at 150 to 250 °C for 18 to 70 h. Oxidation at 150° C yielded a further small increase in flotation between pH 6 to pH 8 as shown in figure 6. These results tend to substantiate Smith's findings (5) that oxidation enhances chromite floatability in the range pH 6 to pH 10. Figure 7 compares the flotation data of the two studies. The trend is clear that controlled oxidation improves chromite flotation in the range pH 6 to pH 10.

OXIDATION POTENTIAL

Figure 8 shows plots of the Eh in the chromite flotation slurries. No direct correlation between oxidation and the Eh is seen in these data. Based on these observations, it was concluded that oxidation of the chromite does not significantly change the Eh. The effect of oxidation on Eh is small because oxidizable components of chromite have vanishingly small solubilities in neutral solutions. However, this does not preclude the possibility that chemically altering the Eh during flotation could substantially affect flotation performance.
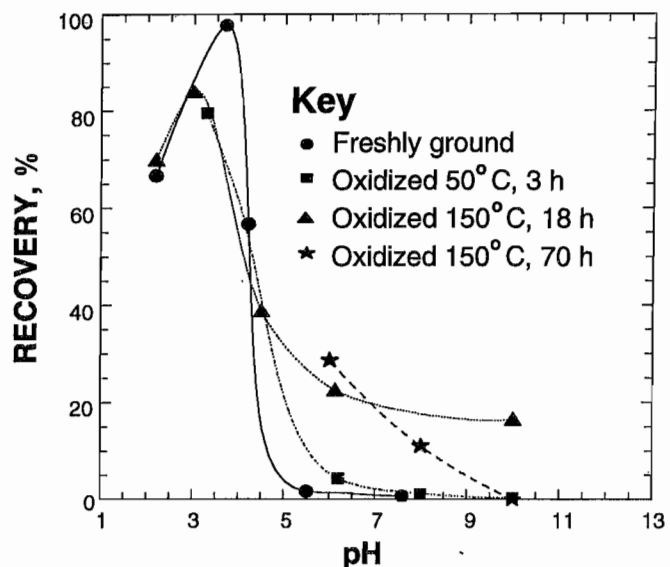
Figure 4
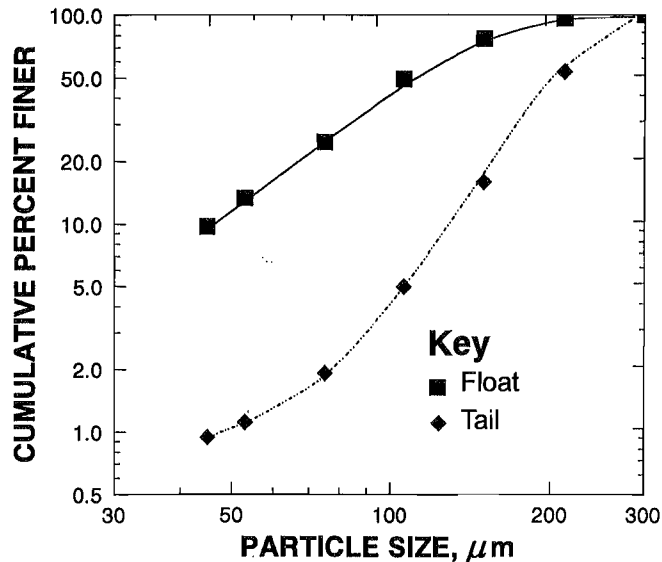
Typical size distributions for float and tail products in the flotation of pure chromite in a Denver cell using SDS collector.

Figure 5
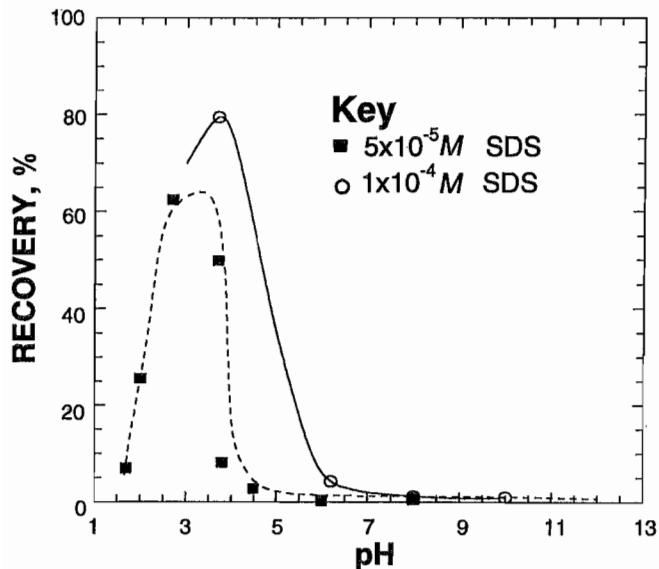
Flotation of oxidized, pure chromite as a function of pH and SDS concentration showing recoveries similar to those of freshly ground chromite (5).

Figure 6

Flotation of chromite following oxidation showing increased chromite floatability above pH 6 following oxidation.

Figure 7
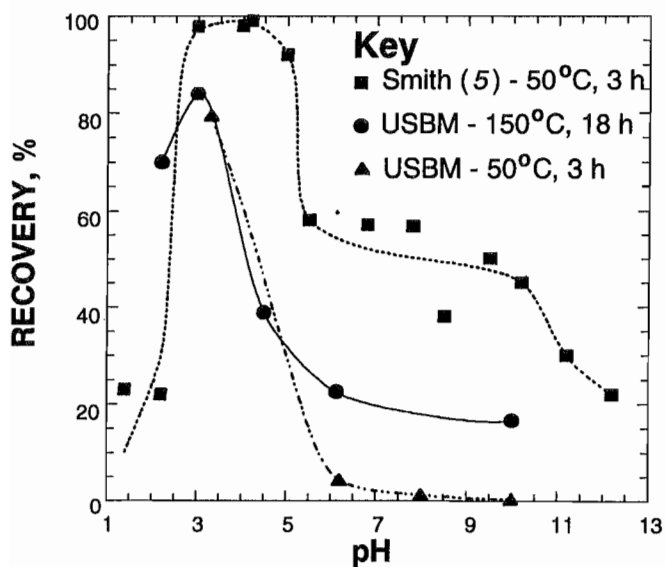
Flotation response of chromite following oxidation showing improved recoveries above pH 6.

Figure 8
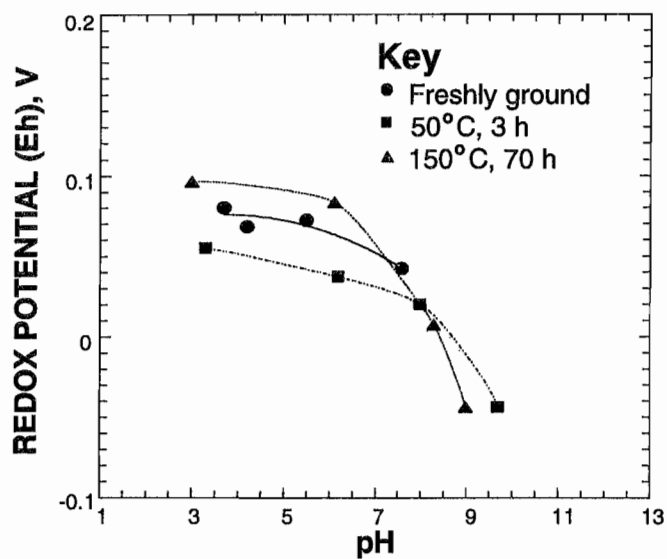
Eh's in chromite flotation slurries during flotation in Denver cell.

OLIVINE FLOTATION

Figure 9 shows the recovery of freshly ground olivine as a function of SDS concentration at pH 4.0 and pH 5.0. The maximum recovery occurred in $5\times10^{-5}M$ SDS at pH 4.0; further increases in SDS concentration up to $5\times10^{-4}M$ decreased olivine flotation. As with chromite, the recovery of olivine is affected by pH; flotation is better at pH 4 than at pH 5 and higher. Flotation of freshly ground olivine in $5\times10^{-5}M$ SDS solution reached a maximum of 28% at pH 4 compared with about 63% flotation of freshly ground chromite at these conditions. The finer olivine fraction floats more readily than the coarser fraction as shown in figure 10.

Olivine recoveries in the present study were lower than recoveries reported by Smith (5). Recovery of freshly ground olivine in a nitrogen-purged Hallimond flotation cell reached a maximum of 61% at pH 4.5, whereas recovery in the Denver flotation cell reached a maximum

of 28% at pH 4. The lower recovery probably is due largely to the coarser size fraction used in the present study (-300 μm compared with 105×149 μm).

Oxidation at 50 °C for 3 h depressed olivine flotation so slightly over most of the pH range that the effect was considered to be insignificant. Data are shown in figure 11. More severe oxidation of olivine at 150 °C and 250 °C for 70 h likewise produced little change in flotation behavior.

OXIDATION POTENTIAL

Typical Eh's in olivine flotation slurries are plotted in figure 12. The Eh was not measurably affected by oxidation over the range pH 3 to pH 11. As with chromite, low solubility of oxidizable species in olivine explains the insensitivity of solution potential to oxidation of the olivine.

Figure 9

Effect of SDS concentration on the flotation of freshly ground olivine at pH 4 and pH 5 in a Denver cell.

Figure 10
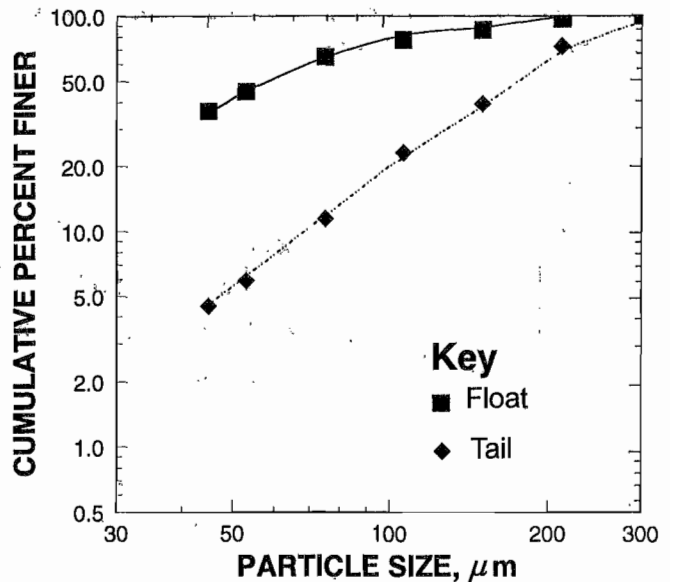
Typical particle-size distributions of float and tail products in the flotation of pure olivine in a Denver cell.

Figure 11
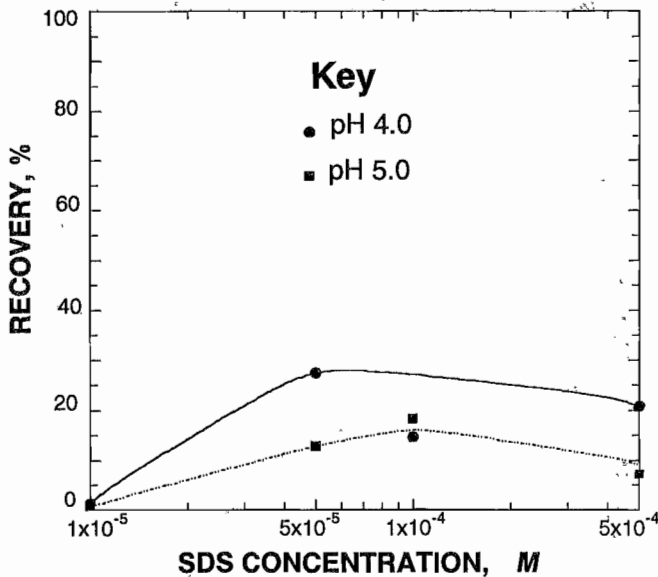

Flotation behavior of pure olivine in $1\times10^{-4}M$ SDS in a Denver cell.

Figure 12

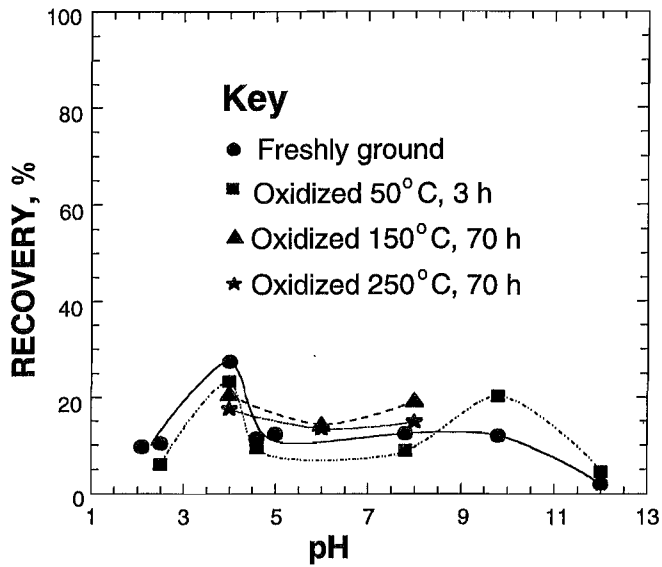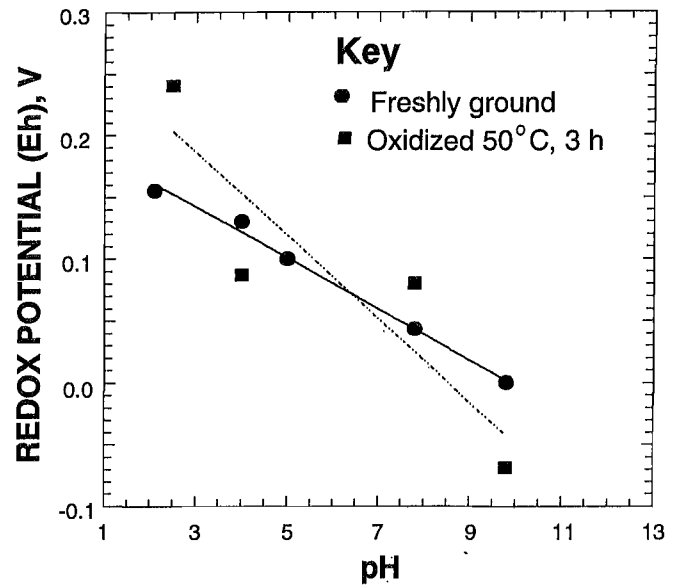*Eh's in olivine flotation slurries in Denver cell tests.*

COMPARISON OF CHROMITE AND OLIVINE FLOTATION BEHAVIOR

The maximum flotation of both chromite and olivine occurs near pH 4. As a result, selectivity in the flotation of freshly ground mixtures is poor. The data show that oxidation does not affect the pH at which maximum recovery occurs. Oxidation, however, affects the flotation behavior of these minerals differently in the pH range 6 to 10. Oxidized chromite tends to float more readily than freshly crushed chromite in this range as seen in figure 6. Flotation of olivine tends to be unaffected or slightly depressed by oxidation over the pH range 2 to 9 as seen in figure 11. This suggests that controlled oxidation followed by flotation in the range pH 4.5 to pH 7 may be useful for selectively separating chromite from olivine.

CHROMITE GRAVITY CONCENTRATE

Several tests were performed to evaluate the possibility that oxidation could be used to improve flotation selectivity of chromite. A chromite gravity concentrate containing both chromite and olivine was used in this evaluation. Analyses of this concentrate are presented in table 2. For convenience, analyses of other relevant samples are included in the table.

Table 2.—Chemical analyses of materials from Smith and current study, weight percent
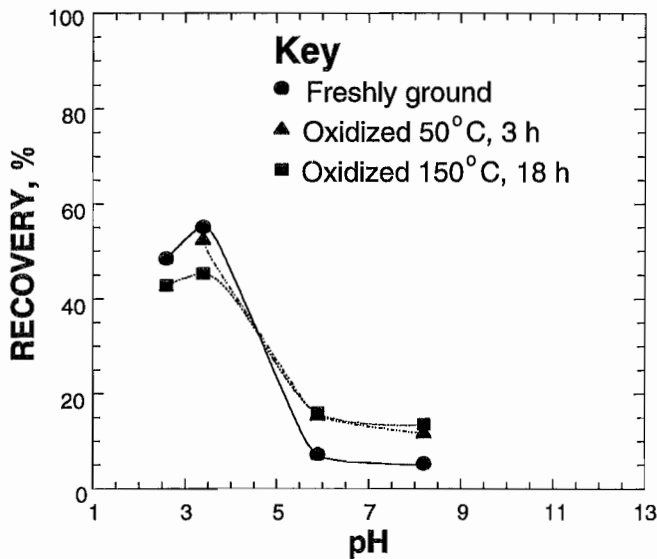
	This study		Chromite concentration	Smith study (5)	
	Chromite	Olivine		Chromite	Olivine
Cr_2O_3 ...	48	NAp	20	42.8	NAp
Fe	23	6	15	22	6
SiO_2	0.6	41.6	20.6	NAp	NAp
Al_2O_3 ...	13.4	0.2	4.7	13.4	0.18
CaO	2.8	2.8	1.2	0.1	0.1
Cr/Fe ...	1.44	NAp	1.34	1.37	NAp

NAp   Not applicable.

Chromite recoveries in the flotation of gravity concentrate samples in $1 \times 10^{-4} M$ SDS are shown in figure 13. Chromite recoveries from the gravity concentrate were lower than those obtained with pure mineral. Recoveries were greatest near pH 4 and became small above pH 5. Oxidation depressed chromite flotation slightly at pH 3 to pH 4. However, oxidation improved chromite recovery in the range of pH 6 to pH 8.

Recoveries in the present study were lower than those obtained by Smith (5) although both studies used chromite from the same deposit. Differences in particle size, mineral chemistry, and flotation apparatus likely caused the lower recoveries in the present study. However, it is significant that oxidation increased recovery in the range of pH 6 to pH 8 in both studies.

Product grade decreased slightly as pH increased from 2.7 in the flotation of freshly ground gravity concentrate as shown in figure 14. Oxidation, however, resulted in marginally improved chromite grades. The optimum selectivity occurred at pH 3.4 where recovery was 53% and grade was 27% Cr_2O_3. Interestingly, the best grade was obtained at pH 3.4 rather than between pH 6 and pH 8 where oxidation has the greatest beneficial effect on chromite floatability. However, very slight improvement in grade was observed following oxidation in the range pH 6 and pH 8.

Obviously, grades and recoveries obtained in this study are far lower than those required for profitable commercial flotation practices. However, the finding that both grade and recovery of chromite benefitted from oxidation is deemed to be significant and may provide the basis for developing a selective separation technique. Further research is needed to demonstrate this finding conclusively.

Typical size distributions of the float and tail products are plotted in figure 15. A finer size distribution was found in the float product as compared with the tail product. These distributions are similar to those for pure chromite.

Figure 13

Flotation recovery of chromite from gravity concentrate in $1 \times 10^{-4} M$ SDS in Denver cell tests.
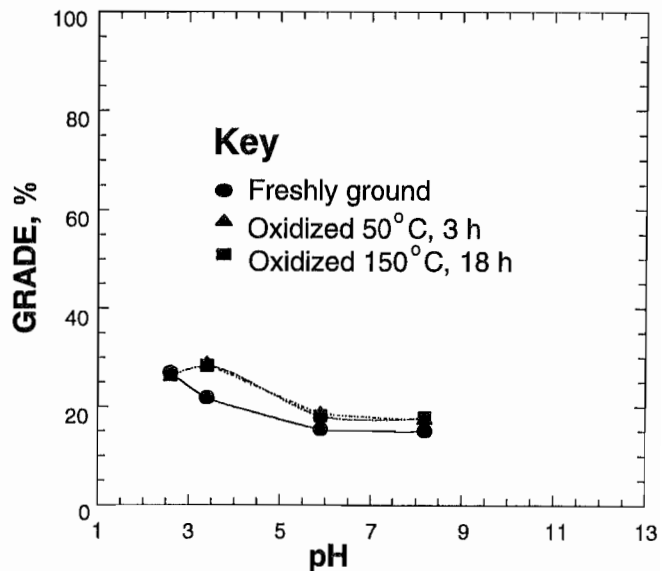
Figure 14

Grade of Cr_2O_3 in the flotation of chromite gravity concentrate in $1 \times 10^{-4} M$ SDS in Denver cell.

Figure 15
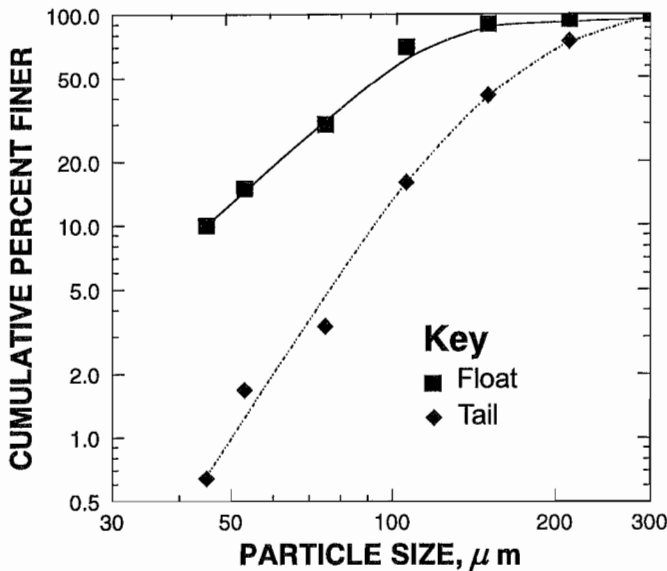
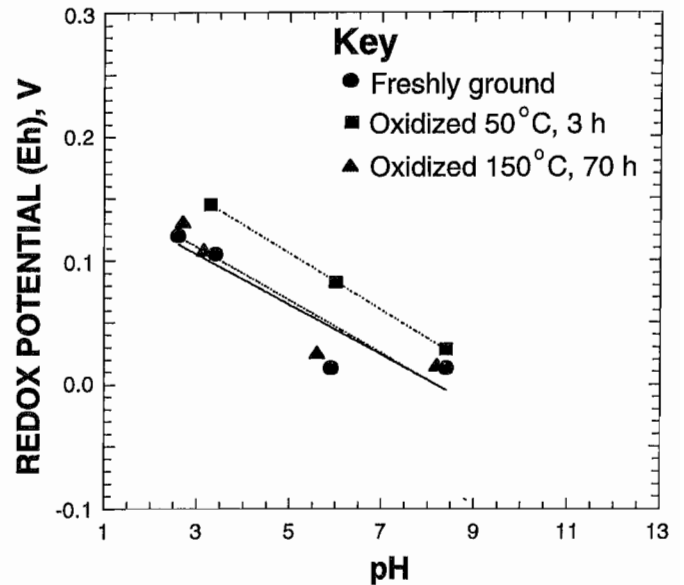*Typical size distributions for float and tail products from flotation of chromite gravity concentrate in 1×10⁴M SDS in Denver cell.*

Figure 16

Eh's in chromite gravity concentrate slurries in Denver cell.

OXIDATION POTENTIAL IN CHROMITE GRAVITY

The Eh's of the gravity concentrate flotation slurries were similar to the potentials found in the flotation of the pure chromite. The Eh was approximately 0.1 V near pH 3 and approached 0 V near pH 9 as shown in figure 16. As in the tests with pure chromite and olivine, no consistent effect of oxidation on flotation slurry Eh was noted. Here again, this is attributed to very low solubilities of oxidizable ions from the minerals.

CONCLUSIONS

Smith observed (5) that chromite flotation could be altered significantly by oxidation of the mineral. The USBM has now completed research to correlate the extent of chromite oxidation with changes in grade and recovery from a domestic chromite resource. Relatively long oxidation times (18 to 70 h) at 150 °C were required to measurably increase chromite floatability. Improved chromite flotation was observed in the pH range of 6 to 8. However, even with a lengthy oxidation treatment the improvement in chromite floatability using SDS flotation collector was small.

Differences in the magnitude of flotation response were apparent between this and an earlier work. These differences are likely due to differences in equipment, chromite composition, and particle sizes. A laboratory Denver flotation cell using air as the flotation gas was utilized in the present study compared with the Hallimond flotation cell with nitrogen flotation gas in the earlier tests. The chromite in the present study had a higher chromium content, which is known to contribute to poor floatability (6). The size distribution was slightly coarser in the present study, which also contributes to low flotation recovery.

This study shows the potential for altering the selectivity in chromite flotation from gangue minerals using oxidation. The effect of oxidation was not as dramatic in the present study as in earlier tests. Additional fundamental studies would be required to adequately understand the effect of oxidation on chromite and olivine flotation. However, controlled oxidation is a novel method that could be employed to enable selective flotation of chromite from siliceous gangue minerals.

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