

Hot Filtration: A Way to Enhance the Recovery of Chromite in Sulfuric Acid Leaching, with or without the Addition of Perchloric Acid

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Abstract

A high grade chromite concentrate obtained from the Pınarbaşı region of Kayseri province in Turkey was reacted with a solution of sulfuric acid and perchloric acid at atmospheric pressure. The effects of temperature, duration, sulfuric acid concentration and perchloric acid addition on leach recovery were determined in several experiments. Hexavalent chromium contents of the final solutions were also analyzed after the experiments and it was found that at the end of leach reaction chromium appeared in the solution as Cr^{3+} and it did not change into environmentally hazardous Cr^{6+} . The final product in the solution was chromium(III) sulfate obtained with about 98.7% maximum recovery, under the optimum leaching conditions of 175 °C, 2 h, 84.6 wt % H_2SO_4 and $1/2$ perchloric acid/chromite ratio.

Key words: Leaching, Chromite, Hexavalent chromium, Sulfuric acid, Perchloric acid.

Introduction

Chromium and chromium chemicals have been playing important roles in our daily lives for years. These are all used for some industrial purposes and they improve some desired features, such as corrosion resistance, in metal and alloy productions. The consumption of chromium in the chemical, refractory, and metallurgical fields is high and increasing rapidly.

Pure metallic chromium, chromium ore or chromite and its trivalent compounds have no harmful effects, that is, they do not have serious effects on body tissues. On the other hand, hexavalent compounds of chromium show an irritating, corrosive and toxic action according to the Materials Information Society (1993).

The mineral chromite is the only commercial source of chromium. Metallic chromium is produced from chromite by pyrometallurgical reduction,

using aluminum, silicon, and carbon as reducing agents, and by electrolysis. After reduction, purity is around 97%-99%, whereas after electrolysis the product contains approximately 99.8% chromium. Besides these techniques, chromite ore or concentrate can be leached with a sulfuric acid solution with minimum amounts of hexavalent chromium in the final leach solution.

There were some similar works done before this study, in addition to the filtration method. Vardar (1993) studied the sulfuric acid leaching of chromite ores in South Africa and Ayhan (2000) performed similar research in Turkey.

Vardar (1993) leached chromite with sulfuric acid and small amounts of perchloric acid. All the experiments were done in a leaching vessel at atmospheric pressure. A solid to liquid ratio of 1:25 and particle size of $-90, +75 \mu\text{m}$ was kept constant in all exper-

iments. Filtration of the leach solutions was done after cooling and dilution.

The results were given as follows at the end of his experiments:

1. When only sulfuric acid was used the highest extraction rate of chromium was 63% at 210 °C, using 77 weight percent sulfuric acid containing leach solution for a leaching duration of 6 h.

2. When perchloric acid was used to improve the rate of reaction, the complete extraction of chromium was obtained at 210 °C, 82 weight percent of sulfuric acid and 1/2 perchloric acid to solid ratio for a leaching duration of 6 h. However, this complete extraction was calculated with the addition of chromium(III) sulfates in the solid residue.

It was also stated that no appreciable hexavalent chromium was obtained.

Ayhan (2000) leached a sample of chromite ore from the Pınarbaşı region of Kayseri province in Turkey with sulfuric acid and perchloric acid. All the experiments were done in a leaching balloon at atmospheric pressure.

Ayhan made the following conclusions after her experiments:

1. In the absence of perchloric acid, the maximum chromium extraction was about 58% under the conditions of 175 °C, 70 vol % H₂SO₄ and 2 h.

2. In the presence of perchloric acid, the maximum chromium extraction was about 83% under the conditions of 175 °C, 70 vol % H₂SO₄, 2 h and 1/2 perchloric acid to chromite ratio.

Ayhan stated that the lower recoveries obtained in her study compared to Vardar's study were most probably due to the different structure of Turkish chromite ores.

The purpose of the present research was to show that it is possible to leach with H₂SO₄ a typical Turkish chromite concentrate supplied by Kromsan, with a high recovery with the use of a new filtration method, and minimum Cr⁶⁺ in solution.

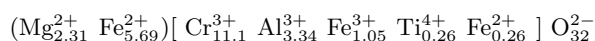
Method and Experimental

The method used in the experiments involved leaching concentrate with sulfuric acid in a glass balloon on a hot plate with stirring and using hot filtration after leaching with Gooch crucibles. In some experiments, perchloric acid was used in addition to sulfuric acid.

In the experiments, chromite ore concentrate from the Pınarbaşı region of Kayseri province in

Turkey, sulfuric acid (95-97 wt % H₂SO₄) and perchloric acid (60 wt % HClO₄) were used as starting materials. XRF analysis of the concentrate was performed at the MTA (Maden Tetkik Arama Enstitüsü) and showed that the concentrate consisted of 47.8% Cr₂O₃, 31.5% Fe₂O₃, 9.70% Al₂O₃, 5.3% MgO, 3.8% SiO₂, 1.0% TiO₂ and 0.2% CaO.

The chemical formula of this chromite was calculated according to the work done in South Africa by Soykan (1991) and is given below:



where the parentheses and the brackets show tetrahedral and octahedral sites, respectively.

The leaching equipment consisted of a hot plate with a magnetic stirrer, a 250 ml glass balloon, a temperature measuring and control probe and a condenser. Figure 1 shows the leaching equipment used in the experiments.

At the beginning of each experiment, sulfuric acid and perchloric acid were mixed with water in the balloon. Heating of the solution was started, and, when the solution reached the desired temperature, chromite was added. Then, after a certain period of time, the hot plate and temperature control were switched off and the solution was immediately filtered via a Gooch crucible (number 4 Gooch crucible) while it was hot. The main difference between the previous studies and this study is at this point. In the previous studies, cooling and dilution were done after the experiments, and so filter paper was used, but in our study hot filtration was used. At the end of the filtration, the leach residue was washed and the pregnant leach solution and wash water were analyzed to obtain the values of chromium recoveries by wet chemical techniques.

The variable parameters investigated in the leach experiments were H₂SO₄ concentration (weight %), temperature, leaching duration and HClO₄ to chromite ratio (volume to weight). The reaction between chromite and sulfuric acid was studied at H₂SO₄ concentrations of 73.4%, 81.1%, 84.6%, 89.3% and 95.2%; at temperatures of 140, 175 and 210 °C; for 2, 4 and 6 h; and at HClO₄ to chromite ratios of 0, 1/4 and 1/2. The parameters taken constant were weight of chromite concentrate as 5 g, solid to liquid ratio as 1:25 and particle size of the concentrate as -38 μm.

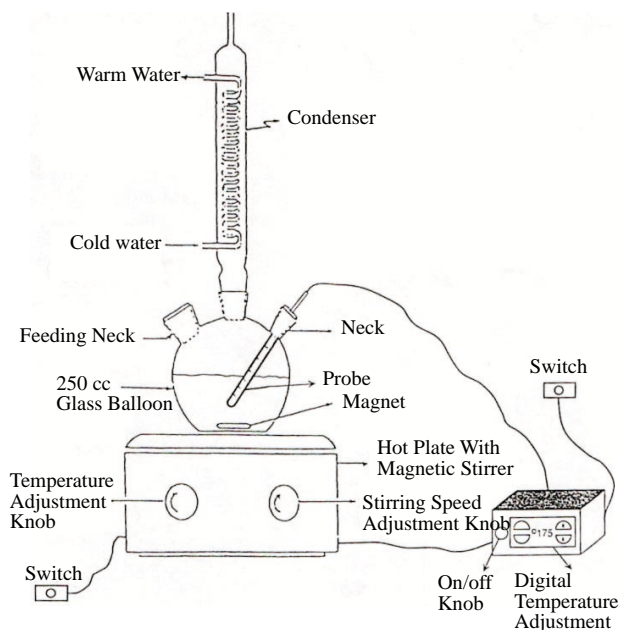
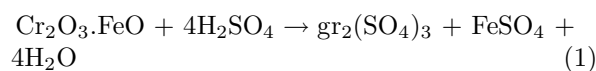


Figure 1. Experimental set-up of the leaching process.

Results and Discussion

Sulfuric acid leaching of chromite without the addition of perchloric acid

The reaction between a simple chromite and sulfuric acid is given by Gupta and Mukherjee (1990) as follows:



However, according to Vardar (1993), since the structure of chromite spinel is more complex than given by this equation, the amount of water molecules and the valency level of aqueous sulfates cannot be known with sufficient accuracy to calculate the stoichiometric amount of sulfuric acid necessary for this reaction. Therefore, the sulfuric acid concentration in the starting leach solutions was chosen to resemble some typical ones encountered in the literature.

The maximum recovery obtainable was about 94.1% after leaching at 175 °C, for 6 h with 84.6 wt % H₂SO₄ solution. Compared to Ayhan's study, this recovery is high under these conditions. This is most probably due to the filtration conditions in the experiments, because the structures of the chromites used in both Ayhan's study and ours were the same. In both of the studies Turkish chromite concentrates

obtained from the Pınarbaşı region were used. As mentioned in the "Method and Experimental" section, hot filtration was used in the experiments. Previous studies were done under the conditions of cooling, dilution and filtration with filter paper.

Effect of acid concentration According to Habashi (1970), the rate of leaching increases with increasing concentration of the leaching agent. However, in our work, this statement is valid only for the condition where the concentration of sulfuric acid was increased from 81.1% to 84.6%. At higher sulfuric acid concentrations, the recovery of chromium decreased, most probably due to the decrease in the reactivity of sulfuric acid at higher acid concentrations. It can be seen in Figure 2 that increasing the acid concentration from 84.6% to 95.2% (by weight), while the temperature and the duration were kept constant at 175 °C and 4 h respectively, decreased the chromium recovery from about 91% to about 53%, by weight.

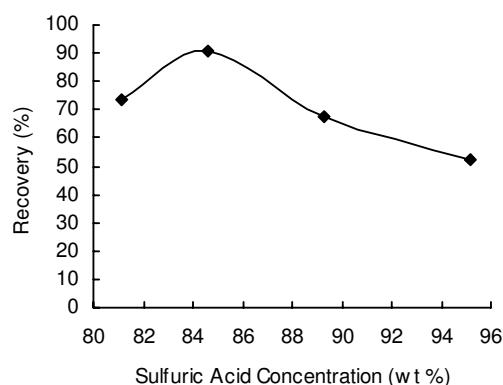


Figure 2. Recovery of chromium as a function of sulfuric acid concentration (duration: 4 h, temperature: 175 °C and no perchloric acid addition).

Effect of temperature The recovery values of chromium as a function of temperature for 2 h leaching duration and using 84.6 weight percent of sulfuric acid containing leaching solution (without addition of perchloric acid) can be seen in Figure 3. The extraction of chromium increased from 58% to 81.1% as the temperature increased from 140 to 175 °C. As the temperature increased, the rate of reaction increased and therefore the extraction of chromium increased. However, when the temperature was increased from 175 to 210 °C, the extraction of chromium decreased by about 2% from 81.1% to 79.2%.

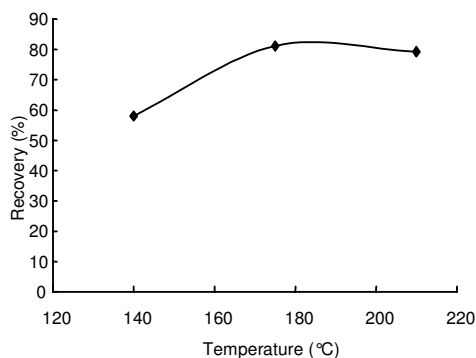


Figure 3. Recovery of chromium as a function of temperature (duration: 2 h, 84.6 wt % of sulfuric acid in solution and no perchloric acid addition).

To explain this case, the solid residues of experiments for 175 and 210 °C were analyzed by scanning electron microscope (SEM). The SEM diagrams obtained (Figure 4) demonstrated some peaks that include chromium in them. Keeping other conditions constant, the intensity of the main peak including chromium increased with increasing the temperature from 175 to 210 °C. Because of these reasons, the mentioned slight decrease in recoveries was most probably due to an increase in the precipitation of chromium.

Effect of leaching duration It can be seen from the results of the experiments that extraction of chromium increases with increasing duration while other conditions are kept constant. This enhancement can be seen from Figure 5. The conditions in the given chart were 175 °C as the temperature, 84.6 wt % sulfuric acid as the concentration and no perchloric acid addition to solution.

When experiments for 2, 4 and 6 h are compared, the highest recovery can be seen for 6 h of duration, i.e. 94.1%. However, in the subsequent experiments, 4 h was chosen as the duration since the recovery values of the experiments for 4 and 6 h were similar to each other. Therefore, it was easier to finalize the experiment in a shorter time.

Sulfuric acid leaching of chromite with the addition of perchloric acid

After the experiments were done using sulfuric acid only, perchloric acid was added to the sulfuric acid to see if the former could increase the recovery values.

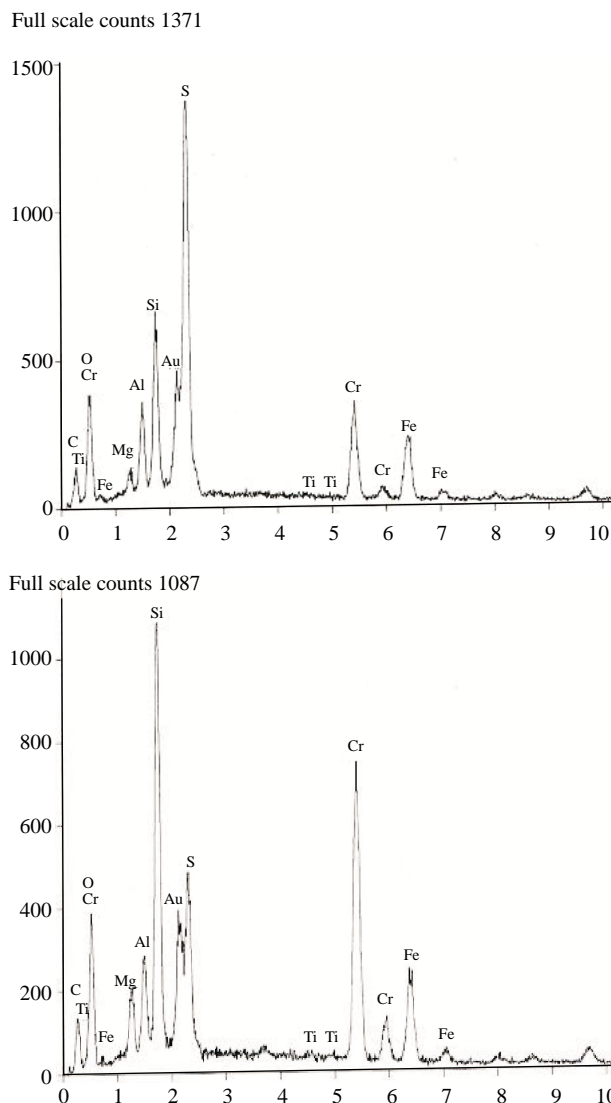


Figure 4. SEM diagrams for 175 °C (above) and for 210 °C (below), keeping other conditions constant.

Effect of perchloric acid addition The extraction of chromium gave the maximum value of 98.7% for the HClO_4 /chromite ratio of $1/2$ for 2 h at 175 °C and for 84.6 wt % of H_2SO_4 .

Figure 6 demonstrates the extraction of chromium as function of perchloric acid to chromite ratio for 2 h of leaching duration, 175 °C and 84.6 wt % sulfuric acid. The recovery values of chromium increased from 81.1% to 98.7% when the perchloric acid to chromite ratio was increased from 0.0 to 0.5. This was most probably due to the fact that perchloric acid increased the decomposition of the chromite by diffusing to the lattice structure (Vardar, 1993).

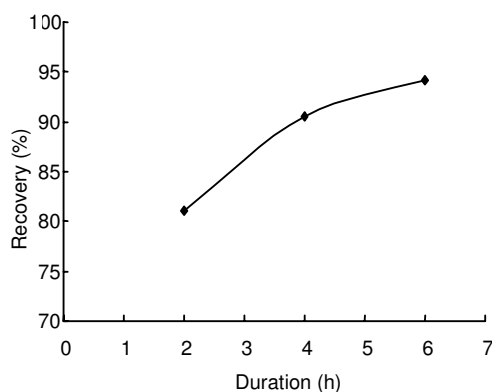


Figure 5. Recovery of chromium as a function of duration (temperature: 175 °C, 84.6 wt % sulfuric acid in solution and no perchloric acid addition).

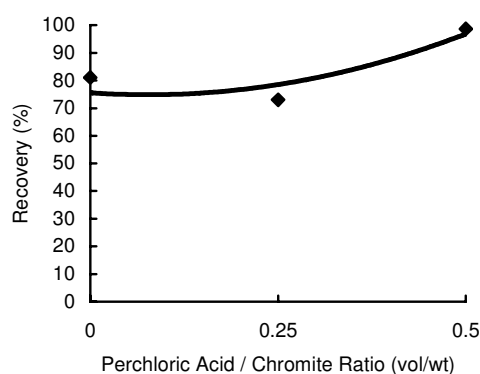


Figure 6. Recovery of chromium as a function of perchloric acid to chromite ratio (temperature: 175 °C, duration: 2 h and 84.6 wt % sulfuric acid in solution).

Effect of leaching duration As can be seen from Figure 7, extraction of chromium decreased from 98.7% to 61.8% as duration increased from 2 to 6 h at 175 °C, 84.6 wt % sulfuric acid and 1/2 perchloric acid to chromite ratio. To explain this decrease, SEM analyses of the residues from the 2 experiments were done and increases in chromium peaks were observed. This meant that lower recoveries found at longer durations were due to the precipitation of some chromium compounds by time with the addition of perchloric acid.

Hexavalent chromium analysis

Four samples were chosen for qualitative chemical analysis. Analyses were done as follows. Certain amounts of samples were taken from the leach solutions. Since the samples were so acidic (pH < 1), their pH value was increased to 1.3-1.5 by mixing

with 20% NaOH with the help of a pH meter because chromium is only seen in this interval. Then 1.5 ml of 0.5% diphenylcarbazide was added to the samples to see the change in the color. If the color is purple-violet, it means that Cr⁶⁺ exists in the sample. Otherwise, no appreciable hexavalent chromium exists.

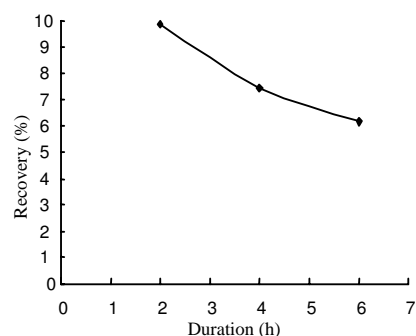


Figure 7. Recovery of chromium as a function of duration (temperature: 175 °C, 84.6 wt % sulfuric acid in solution and 1/2 perchloric acid to chromite ratio).

If hexavalent chromium was found in the samples, quantitative analysis was done. Samples of experiments 1, 2 and 3 were chosen to see the change in Cr⁶⁺ amount with duration on a chart if hexavalent chromium was present in the solutions. Furthermore, the experiment that had the highest extraction value was chosen. However, in the chemical analyses, hexavalent chromium was not found in sample solutions.

These results are important and indicate the success of the method since there was no hexavalent chromium in the leach solutions.

Conclusions

In this research the sulfuric acid leaching of a typical Turkish chromite concentrate was studied under hot filtration conditions chosen as the filtering unit. The following conclusions were drawn based on the experimental results:

1. In the absence of perchloric acid, the maximum chromium extraction was 94.1% under the conditions of 175 °C, 84.6 wt % of H₂SO₄ and 6 h.
2. In the presence of perchloric acid, the maximum chromium extraction was 98.7% under the conditions of 175 °C, 84.6 wt % of H₂SO₄, 2 h and 1/2 perchloric acid to chromite ratio.
3. The extraction values for both cases of with or without perchloric acid were higher than those obtained by Vardar (1993) and Ayhan (2000). This was

most probably due to the use of different filtration technique. The structures of the chromites used in both Ayhan's study and this one were the same, only one parameter was different when these 2 studies are compared, i.e. filtration technique. The solutions obtained in this work were filtered while they were hot. However, the filtration in the previous studies was done after cooling and dilution.

4. Perchloric acid addition increased the chromium recovery to its maximum value for the shortest time used during the experiments by its contribution to the decomposition of chromite due to its high oxidation potential. However, the effect of perchloric acid on chromite is not very obvious in the literature.

References

Ayhan, E., "Sulfuric Acid Leaching of Turkish Chromite Ores", Master Thesis, METU, Ankara, 2000.

Gupta, C.K. and Mukherjee, T.K., *Hydrometallurgy in Extraction Processes*, CRC Press, USA, 1990.

Habashi, F., *Principles of Extractive Metallurgy, Hydrometallurgy*, Gordon and Breach, 1970.

Soykan, O., Eric, R.H. and King, R.P., "The Reduction Mechanism of a Natural Chromite at 1416 °C",

Metall. Trans., 53-63, 1991.

The Materials Information Society, "ASM Handbook", Volume 2, "Properties and Selection: Non-ferrous Alloys and Special Purpose Materials", Tenth Edition, 1993.

Vardar, E., "Acid Leaching of Chromite", Master Thesis, University of Witwatersrand, Johannesburg, 1993.