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Recovery of $MnSO_4$ from Low-Grade Pyrolusite Ores, and of $MnSO_4$ and Silver from Manganese-Silver Ores

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ABSTRACT

The aim of this study was to economically recover $MnSO_4$ from low-grade manganese ores, abundantly available in the Southeastern Anatolia Region, and $MnSO_4$ and silver from manganese ores containing silver. In the research carried out thus far, an economical method aimed at treating these ores has not been found. In this study, the recovery of $MnSO_4$ from low-grade manganese ores was realized. The $MnSO_4$ recovered was fairly pure. Our method was then applied to manganese-silver ores; fairly good results were obtained. The silver which remained in the residue following production was taken into a solution medium. In the first stage of our research, studies on pyrolusite ores containing 36.98% manganese were conducted. Ninety-one percent of the manganese was taken into solution as $MnSO_4$ by providing proper conditions (the experiment was carried out with a mixture of 1.8175 g sawdust, 9.1 mL of 96% H_2SO_4, and 15.7750 g pyrolusite). In the second stage, 94.0% of the manganese existing in used silver-pyrolusite ore was taken into solution as $MnSO_4$ (the experiment was carried out with a mixture of 73.850 g pyrolusite, 9.9646 g sawdust, and 98.2 mL of 96% H_2SO_4). In this study the amount of silver passed into solution was found to be 3.73%. The 97% manganese passed into solution was crystallized as $MnSO_4 \cdot H_2O$, and its degree of purity was determined to be 96.0%. The remaining residue was extracted with thiourea at an extraction time of 30 minutes. Also, 98.1% of the silver and all of the gold were taken into solution. When the silver and gold taken into solution were exposed to adsorption with activated carbon, they were adsorbed within $2\frac{1}{2}$ hours. The thiourea had not been degraded within this time period.

INTRODUCTION

Most countries recover their manganese compounds from low-grade ores because they do not possess high-grade ores. Turkey has 28 million tons of low-grade manganese ores. Flotation and magnetic separation methods for the enrichment of these ores have not been successful. Therefore, improved hydrometallurgical methods need to be developed.

In order to obtain the concentrated manganese needed by the metallurgy industry, some hydrometallurgical methods have been found and applied. These are extractions by SO_2, NO_2, and acidic solutions, and leaching with Fe^{2+} solution in an acidic medium.

In addition, pyrolusite can be reduced with coke and lignite or diesel oil. The manganese oxide which results can be extracted with H_2SO_4, but this method has many disadvantages. In particular, it causes Fe_2O_3 (found in ferrous manganese ores) to be reduced to FeO, and the separation of this compound from manganese is economically difficult. These difficulties may be eliminated if the reduction process is carried out with gaseous reductants at a low temperature.

During the recovery of $MnSO_4$, poplar sawdust was used as the reductant. Poplar sawdust was chosen for two reasons. First, it has very little ash and its cellulose level is high. Second, it is widely found in our region and can be provided very cheaply. Sawdust obtained from other trees also was used, but the results were not as good as those of poplar sawdust; i.e., the purity of recovered $MnSO_4$ was lower and the yield was smaller.

EXPERIMENTAL

In this study, research was carried out on two different samples. The first was a low-grade manganese ore provided from the region where the Kralkizi Dam is located. Recovery of $MnSO_4$ was realized from this sample. The second sample was a manganese-silver ore found in the Elazig-Keban area. Recovery of $MnSO_4$ as well as silver was provided from this sample.

For analysis of pyrolusite, determination of manganese was carried out by the Wolhard method, that of total iron by the dichromate method accompanied by diphenyl sulfonate indicator, and that of calcium oxide and magnesium oxide by the oxalate and pyrophosphate methods, respectively. Processes to obtain the silicon dioxide in a pure state from the sample were carried out, and then pure SiO_2 was precipitated. It was brought to constant weight, weighed, and after removing it from the medium, it was weighed again, and the difference between the two weights was determined as SiO_2. The processes were conducted in a platinum crucible.

Recovery of $MnSO_4$ from Kralkizi Dam Pyrolusite Ores

Prior to carrying out the experiments, the moisture and ash content of the poplar sawdust used as reductant were determined. The moisture content was 5.84% and the ash content was 1.98%. In the experiments, pyrolusite of 100–160 mesh and sawdust of −60 mesh were used.

The analysis results of pyrolusite are given in Table 1. In all the experiments, pyrolusite and sawdust were initially stirred until they became homogeneous, and then the reactor was placed on a heater. H_2SO_4 (96%) was added drop by drop, and the mixture was stirred in the course of the reaction. The reaction occurred between 200 and 240°C. Since the reaction was exothermic, the temperature reached about 160°C following the addition of H_2SO_4. In order to keep the temperature between 200 and 240°C, a heater was used.

The material amounts used to carry out the experiments were identified by taking into account the following reaction (5) equation:

$$12nMnO_2 + (C_6H_{10}O_5)_n + 12nH_2SO_4 \rightarrow 12nMnSO_4\cdot H_2O + 6nCO_2 + 5nH_2O \quad (1)$$

All the experiments were conducted twice, and the results were evaluated accordingly.

The experiments were carried out in a 400-mL glass beaker. The mixture was left to cool by retaining it for given periods between 200–240°C. After leaching with water, the solution was put into a 250-mL flask. The determination of Mn^{2+} was accomplished from the solution.

In the first experiment, 29.8496 g pyrolusite, 3.4398 g sawdust, and 17.7 mL H_2SO_4 (96%) were taken, and the mixture was held at a temperature

TABLE 1
Chemical Composition of Kralkizi Pyrolusite Ore

Compounds	Amounts (%)
Mn	36.98
Fe	0.37
CaO	0.11
MgO	0.10
SiO_2	8.60

between 200 and 240°C for 30 minutes. When a determination of the manganese that passed into solution was carried out, it was found to be 29.6%.

In the second experiment, the mixture of 18.3 mL water and 18.3 mL H_2SO_4 (96%) was added dropwise into a mixture of 30.9390 g pyrolusite and 3.5653 g sawdust. The yield was 59% when the sample, obtained as a result of the same time period and temperature, was leached with water, and the manganese that passed into solution was determined.

The change in yield is due to the different concentrations of H_2SO_4 used in these two experiments.

In the third and fourth experiments, in addition to sawdust, $FeSO_4$ and 0.1 M H_2S solutions were included as reductants. When experiments were carried out separately, it was found that the manganese amounts were 82 and 81%, respectively, as a result of studies performed under the same conditions. The third experiment was conducted by adding 28.44 mL of 1.0497 M $FeSO_4$ to the mixture of 15.8104 g pyrolusite, 1.8219 g sawdust, and 9.4 mL H_2SO_4 (96%). The fourth experiment was carried out by adding 204 mL of 0.1 M H_2S solution to the mixture of 15.1926 g pyrolusite, 1.7507 sawdust, and 9 mL H_2SO_4 (96%).

The $FeSO_4$ and H_2S amounts taken for the third and fourth experiments had rates equivalent with that of manganese which could not be taken into solution in the second experiment. This was calculated according to the following reactions:

$$MnO_2 + 2Fe^{2+} + 4H^+ \rightarrow Mn^{2+} + 2Fe^{3+} + 2H_2O \qquad (2)$$

$$MnO_2 + H_2S + 2H^+ \rightarrow Mn^{2+} + S + 2H_2O \qquad (3)$$

Since the desired result was not obtained in any of these experiments, the influence of the time on experiment yield was carefully examined.

In the fifth experiment, 9.0 mL H_2SO_4 (96%) was added dropwise to a mixture of 15.7750 g pyrolusite and 1.8175 g sawdust; it was left at 200–240°C for 45 minutes. Later, after adding 9.4 mL deionized water, it was again left at the same temperature for 45 minutes and stirred constantly during this period. The mixture was left at the same temperature for an additional 90 minutes without stirring. At the end of experiment, it was found that the yield of manganese passed into solution following the leaching process with water was 91.0%.

Posterior experiments were conducted on pyrolusite-silver ores.

Recovery of $MnSO_4$ and Silver from Keban Pyrolusite-Silver Ore

The analysis of manganese, iron, calcium oxide, magnesium oxide, and silicon dioxide in Keban pyrolusite-silver ore was achieved by the same methods applied to the sample from Kralkizi pyrolusite. Au and Ag were analyzed with an atomic absorption spectrophotometer. Analysis results are given in Table 2.

The first experiment was conducted by using experimental conditions in which $MnSO_4$ from Kralkizi pyrolusite ore was included in the solution at its maximum level. For this, 52.8283 g was stirred thoroughly with 7.1279 g sawdust, and then 23.5 mL H_2SO_4 (96%) and 23.5 mL water were added dropwise. The mixture was stirred continuously for 90 minutes at 200–240°C. The amount of manganese that passed into solution was found to be 68.0%.

In the second experiment, the amount of H_2SO_4 was doubled while all other quantities and conditions were kept constant. The amount of manganese that passed into solution was determined to be 91.0%.

In the third experiment, the amount of sawdust was doubled while keeping the conditions and other quantities used in the second experiment the same. The amount of manganese was again 91.0%.

The next time, the amount of acid was doubled and the experimental conditions used for the second experiment were used again [mixture of 73.8520 g pyrolusite sample, 9.9646 g sawdust, 98.2 mL H_2SO_4 (96%), and 98.2 mL water]. The amount of manganese that passed into solution was 94.0%, and 3.73% silver passed into $MnSO_4$ solution under these experimental conditions.

After this result, the recovery of silver from the residue and that of $MnSO_4$ solution through crystallization were dealt with.

Crystallization of $MnSO_4$ Passed into Solution

To obtain pure $MnSO_4$ crystals, $MnSO_4$ solution from the fourth experiment was used.

TABLE 2
Chemical Composition of Keban Silver-Pyrolusite Ore

Compounds	Amounts
Mn	27.11%
Fe	22.60%
SiO_2	4.27%
MgO	0.12%
CaO	0.10%
Ag	218 g/ton
Au	1 g/ton

The following processes were carried out, taking 50 mL samples out of the solution which had a total volume of 1 L. The solution was stirred continuously and boiled. The pH of the solution was then brought to between 3 and 4 by using $Ca(OH)_2$. Fe^{3+} ions precipitate as $Fe(OH)_3$ within this pH interval, but manganese remains in solution. Following the separation of $Fe(OH)_3$ from the solution, it was boiled until the formation of the first $MnSO_4$ crystals. After cooling the solution, $MnSO_4$ crystals were filtered in a Gooch crucible, followed by heating again. The precipitated $MnSO_4$ crystals were refiltered. This process was repeated until the entire solute was removed. The crystals which were obtained were combined and kept in an oven at 290–300°C until they reached constant weight. The $MnSO_4$ obtained had a purity of 96.0%, and 97.0% of the manganese in the solution had crystallized.

Recovery of Silver from Pyrolusite-Silver Ore, the Manganese of Which Was Removed

In this study, a thiourea solution was used for the extraction of silver. For this, pyrolusite-silver samples from which manganese was removed were used.

The first experiment was conducted on a sample from which 68.0% of the manganese had been removed. Two separate pieces weighing 17.0455 g were taken out of this sample. They were dried at 110°C for 2 hours to bring them to constant weight.

The sample was placed into the reactor shown in Fig. 1. Two hundred milliliters of thiourea solution (5 g/500 mL) was added and the pH was adjusted to 1 by the addition of H_2SO_4. The experiment was carried out at 40°C. A pH meter, a reverse cooler, and a thermostat adjusted to 40°C were attached to the reactor. The extraction process was carried out for 5 hours. Every hour a sample was taken and analyzed. The maximum value was determined after an hour, and then there was a decrease in silver extraction yield. The maximum extraction yield was 65.2%.

In the second experiment using pyrolusite-silver ore, 91.0% of the manganese was removed. The study was carried out under the same conditions as those of the first experiment, and the identification of silver passed into solution was followed by taking a sample every half an hour. The maximum extraction yield was reached at the end of the first half hour; this value was determined as 87.9%.

In the third experiment using the pyrolusite sample, 94.0% of the manganese was removed. This experiment was conducted under the conditions applied in the first two experiments. A sample was taken every 15

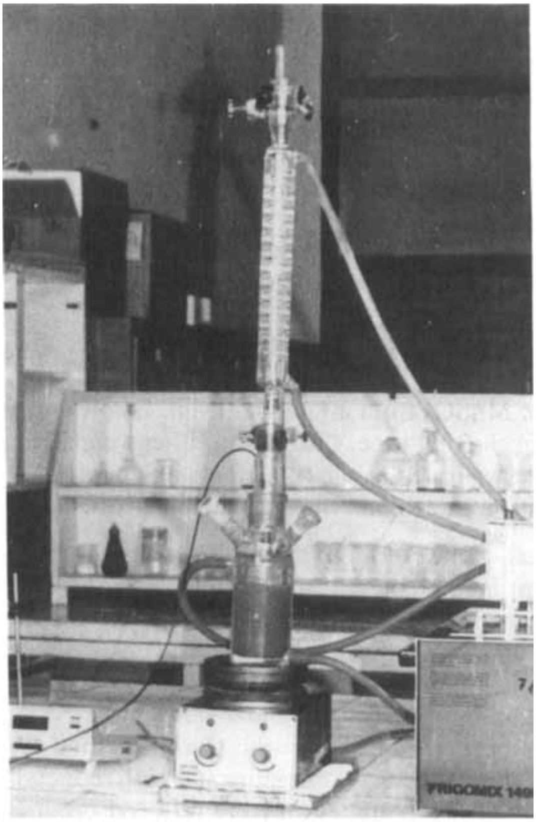

FIG. 1 The apparatus in which the experiments were conducted.

minutes and analyzed; the maximum extraction yield was reached in the first half hour. The amount of silver which had passed into solution at the end of the first half hour was determined as 98.1%. Moreover, during this period all the gold passed into the solution. After the optimum conditions for gold and silver extraction had been determined in this manner, the economic aspect of the process was investigated. For this, thiourea consumption needed for 1 ton of ore was determined. The free concentration of thiourea was determined by titration with 0.05 M $Hg(NO_3)_2$ accompanied by diphenylcarbazide as the indicator. It was determined that approximately 9.5 kg thiourea was consumed for 1 ton of ore, starting with the thiourea that remained in the solution without degradation.

Separation of Silver Taken into Thiourea Solution

This process was carried out through active coal adsorption. For this, 249.8 mg Ag/g C was used (6). The experiment was conducted at 25°C with continuous stirring. A sample was taken every half hour and analyzed. At the end of $2\frac{1}{2}$ hours practically all of the gold and silver in the solution was adsorbed, and the thiourea in the solution was not degraded at the end of this period.

No gold and silver remained in the solution medium according to analysis with a Varian Techtron 1200 Model AAS.

DISCUSSION

Recovery of $MnSO_4$ from a Kralkizi Dam sample was realized through this method for the first time. In addition, Cheap and abundantly available poplar sawdust was used as the reductant. The consequences of the studies carried out on the Keban manganese-silver ores are as follows.

1. Neither manganese nor silver can be concentrated through physical enrichment methods (7).
2. Only 38% of the silver could be extracted by the direct cyanidation method.
3. Recovery of silver by the amalgamation method is not possible due to the pollution of mercury by manganese (8).
4. Silver has been recovered by the Caron method (9) in yields of 85 and 88%. The reducing temperature at which reductant gases are most effective is 550°C (sufficient for the reduced products to be leached with a 1% NaCN solution during 7 hours). In cyanidation, 3–3.28 kg CaO and 1.66–2.5 kg NaCN are consumed for each ton of reduced product. In the extraction of products with cyanide reduced by this method, gold and silver are dissolved but other elements are not. In this way, clean cyanide solutions are produced. Recovery of manganese from the residue obtained after extraction of NaCN by this method seems possible neither by physical methods nor by being dissolved with H_2SO_4.
5. Under optimum conditions for the McClusky method, manganese and silver could be extracted in yields of 94.48 and 86.0%, respectively. Extraction by SO_2 at a specific pH of the medium dissolves manganese, iron, calcium, magnesium, and zinc. It is also possible to produce $MnSO_4 \cdot H_2O$ from this solution. Following the extraction of pyrolusite with SO_2, 14.72 kg CaO and 2.5–2.8 kg NaCN are consumed per ton of residue. The cyanide solution obtained by this method is less pure than that obtained by the Caron method. How-

ever, gold and silver can be recovered from this solution by being adsorbed and reduced by active coal.

6. Silver was extracted with thiourea leaching at a maximum yield of 78.16% from the residue from which manganese was removed by the SO_2 process. For 1 ton of residue, 25 kg thiourea was consumed (10).
7. To recover manganese from manganese-iron beds, there are such methods as melting (11), developed by the US Bureau of Mines, roasting (12, 13), extraction by SO_2 (14) and H_2SO_4-$FeSO_4$ solution (15, 16), as well as the production of $MnSO_4$ with sawdust from low-grade pyrolusite ores in the Thrace region of Turkey (17). The kind of sawdust used was not reported in the last study.

CONCLUSIONS

The following results were obtained by the method applied in this study.

1. It is possible to put over 90% of the manganese into solution and to produce $MnSO_4$ in over 96% purity.
2. The 94.0% manganese which manganese-silver ores contain was leached. In addition, the facts that the reaction occurs in the 200–240°C interval and that the reaction is complete in 30 minutes are favorable economic aspects of the method. Moreover, because the reaction is exothermic, the temperature of the medium becomes 160°C by itself, and so the desired temperature interval is easily reached.
3. The yield provided in the extraction of silver with thiourea from the residue, from which manganese was removed, is about 98%. All of the gold in the ore is extracted together with the silver.
4. The thiourea consumed per ton of pyrolusite in thiourea extraction was determined to be 9.5 kg.
5. Poplar sawdust, used as a reductant for taking the manganese into solution, is cheap and abundant, another significant economic factor. Accordingly, pure $MnSO_4 \cdot H_2O$ is obtained by this method without the need for complex and costly systems. Gold and silver, which manganese-silver ores from the Keban region contain, can be obtained by an economic and easily applicable method.

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