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HYDROMETALLURGICAL BENEFICIATION OF MANGANESE ORE FROM SINAI

High grade manganese ore constitutes up to 30% of the feed stock of welding flux (calculated as MnO_2). The Fe and S contents in the ore should not exceed 1.7% and 0.02%, respectively. The available medium grade Mn ore from Sinai used in this study contains about 7% Fe and 0.4% S which renders it unsuitable for this purpose.
Magnetic separation of the ore is not an economical method for the removal of these deleterious elements due to the complex nature of the ore. It was found that direct leachimg of the ore with sulphuric acid is an effective method to reduce Fe content to the required limit, S being removed by successive washing. The leaching process as systematically studied and the optimal conditions were achieved. Consequently, pilot plant production was carried out using a 600 dm^3 capacity reactor. The process is successful in reducing the Fe and S contents to satisfactory limits of 1.6% and 0.019%, respectively.

INTRODUCTION

Natural high grade manganese ores (82% MnO_2) are used in the manufacture of welding fluxes. The presence of Fe_2O_3 in the manganese silicate welding fluxes influences the arc stability, viscosity and penetration properties of the welding fluxes (Schwemmer et al., 1978). The ore should contain less than 2.5% Fe_2O_3 and 0.02% S. In Egypt, appreciable amounts of such ore were imported by welding flux producers as the local manganese ores contain high iron admixtures. Several trials were made to remove iron from local ores by physical processes, e.g. magnetic separation (CMRDI, 1989). Removal of iron by reduction followed by magnetic separation was accompanied with appreciable losses of manganese dioxide in the magnetic fraction due to the presence of iron oxide disseminated in the manganese dioxide crystal lattice. The present investigation aims at the removal of iron oxides from the local ore from Sinai with 70% MnO_2 and 11% Fe_2O_3 by a hydrometallurgical process using sulphuric acid.

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EXPERIMENTAL

Material

0.5 t of the medium grade manganese ore from Sinai and commercial grade 98% sulphuric acid supplied by Abu-Zaabal Fertilizer and Chemical Company were used in this study. Magnafloc 350 flocculant ofAllied Colloids Co. was used in the settling tests.

Procedure

For ore characterization the sample was ground to - 200 mesh and chemically analysed using the standard chemical analysis procedure (Young, 1971). X-ray diffraction analysis was carried out using AD-500 Siemens diffractometer with Ni-filtered Cu-radiation. Leaching tests were carried out in a 250 cm^3 round bottom flask placed in a thermostat. Manganese ore was added gradually to the reaction vessel containing sulphuric acid while stirring. After the elapse of the reaction time, the slurry was filtered on Whatmann filter paper No. 42, washed thoroughly with distilled water till free of acidity, dried and analysed for iron content. Settling was also examined with and without the addition of flocculant using a 500 cm^3 measuring cylinder. Pilot plant production was carried out in a 600 dm^3 rubber--lined tank. Heating was effected by silica-coated immersion heaters connected to temperature control unit which kept the temperature at 90 °C. The slurry was agitated by side-fixed (angular) agitator (Fig. 1). After the elapse of the reaction

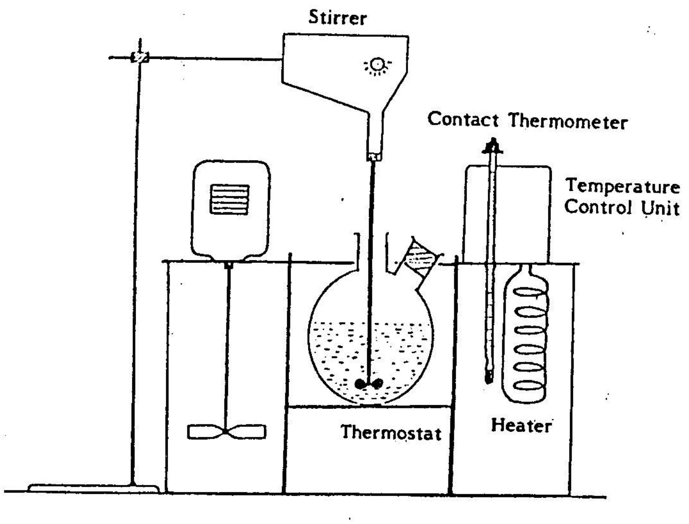

Fig. 1. The reaction system

time, the slurry was transferred to three settling tanks arranged in cascade system. The solid was washed with water by settling and decantation till free of acidity. The washed thick slurry was transferred by a slurry pump to a vacuum filtration system which consisted of a rotary drum filter, receiving tank and vacuum pump. The product was finally dried at 110 °C in a pilot shelf drier.

RESULTS AND DISCUSSION

1. Characterization of the Manganese Ore Sample

The ore contained: MnO_2 (70.30%), Fe_2O_3 (10.35%), SiO_2 (1.65%), P_2O_5 (2.28%), Al_2O_3 (1.05%), MgO (0.10%), CaO (4.95%), S (0.32%). The chemical analysis of the sample, shows that the manganese ore sample was a medium grade material with high contents of impurities, mainly, Fe_2O_3, CaO, S and P.

X-ray diffraction data showed that the ore is composed mainly of pyrolusite admixed with small amounts of hydrated iron oxide FeOOH and dolomite $CaMg(CO_3)_2$.

2. Leaching

a) Effect of H_2SO_4 concentration

To determine the effect of acid concentration on iron removal, a series of experiments was carried out at 90 °C for 2 hours using different acid concentrations (20–40%) at 13 weight percent of solid. It can be noticed from Table 1 that increasing acid concentration from 20% to 30% decreases the iron content in the sample from 2.7% to 2.29%. Further increase in acid concentration does not lead to a pronounced decrease of the iron content, therefore, the optimal acid concentration is 30%.

b) Effect of temperature

A series of experiments was performed using 30% sulphuric acid for 2 hours at 13% solids content and at different reaction temperatures to know the effect of temperature on the removal efficiency of iron. It can be noticed from Table 2 that the increase of temperature increases the extent of iron removal reaching its maximum equal to 68.54% at 90 °C at which the remaining iron content is 2.29%.

Table 1. Effect of acid concentration on the removal of iron in the pyrolusite sample. Initial Fe content was 7.28%

Acid concentr., %	Fe, %	Iron removal
20	2.70	62.9
30	2.29	68.5
40	2.19	69,9

Table 2. Effect of temperature on the removal of iron from the pyrolusite sample. Conditions: 2 hours, 30% H_2SO_4, 13% solids content. Initial Fe content was 7.28%

Temperature, °C	Fe,%	Iron Removal,%
70	3.57	50.99
80	3.13	57.06
90	2.29	68.54

c) Effect of leaching time

A series of experiments was carried out at 90 °C using 30% acid at 13% solid content for different times of leaching (2–8 hours) to show the effect of the time on the extent of iron removal. Table 3 shows that iron removal from the treated sample is significantly increased by increasing the time of leaching reaching about 1% iron content after 8 hours. It may be noticed also that after 6 hours the iron content is 1.56% which is practically acceptable for welding flux production. Therefore, the optimal duration time of leaching is 6 hours.

d) Effect of solids content

A series of experiments was performed at 90 °C using 30% acid, each time for 6 hours at different solids contents (13–20%) to determine the effect of solid content on the extent of iron removal. Table 4 shows that increasing solid content decreases the efficiency of iron removal due to the decrease of the amount of 30% sulphuric acid. From the mentioned results it is noticed that the dissolution of iron from manganese ore is largely dependent on temperature and duration time of leaching.

e) Optimisation of the leaching process

A maximal iron removal of 78.57% is achieved under the following conditions: acid concentration 30%, temperature 90 °C, time of leaching 6 hours, solids content 13%. Under these conditions Fe_2O_3 content in the pyrolusite sample decreased from 10.35% to 2.23%.

Table 3. Effect of duration of leaching on the iron removal from pyrolusite sample. Conditions: 90 °C, 30% acid, 13% solids content. Initial Fe content was 7.28%

Time, hr	Fe, %	Iron removal, %
2	2.29	68.54
3	2.05	71.84
4	1.91	73,76
6	1.56	78.57
8	1.00	86.26

Table 4. Effect of solid content on the removal of iron from pyrolusite sample. Conditions: 90 °C, 6 hours, 30% acid. Initial Fe content was 7.28%

Solid content, %	Fe, %	Iron removal, %
13	1.56	78,57
17	2.30	68.41
20	2.48	65.93

3. Solids separation and washing

a) Filtration

Separation of the treated manganese ore from the leaching liquor was performed by vacuum filtration using a Buechner-type funnel filter 9.2 cm in diameter. The filtration was performed at different pressure differences equal to 250, 430 and 600 mm Hg. It was observed that the filtration rate significantly increased from 42 to 102 cm^3/min. by increasing the pressure difference from 250 to 430 mm Hg while a further increase in the pressure difference decreased the filtration rate to 90 cm^3/min. at 600 mm Hg. At such high pressure difference the manganese cake is compressible; fine particles fill the voids formed between the larger particles thus increasing the cake resistance and consequently decreasing the filtration rate. In general, mentioned filtration rates are very low. Washing the sample till free from acidity required eight washing steps. Filtration and washing processes require long time and large filter area. Thus, it is suggested to study the solid/liquid separation by settling and decantation.

b) Settling and decantation

The results of settling rate measurements indicated that the average settling rate was 0.87 cm/min. without flocculant. The rate increased 4 times (3.5 cm/min.) by using the non-anionic flocculant Magnafloc 350. The optimal doze of the 0.1% flocculant is 5 cm^3 for 500 cm^3 slurry containing 100 g solid. One cm^3 flocculant is required for decantation of 500 cm^3 slurry. It was found that the removal of free acidity requires 8 steps which will require (for 500 cm^3 slurry) 8 cm^3 of 0.1% flocculant and consequently the overall decantation process require 13 cm^3 of 0.1% flocculant which is equivalent to 130 g flocculant per ton of the solid.

4. Pilot plant production

A 100 kg sample was leached in a 600 dm^3 tank. The calculated amount of water was added followed by gradual addition of the ore using rock feeder while agitating. The required amount of 98% sulphuric acid was gradually added by a dozing pump to obtain 30% acid concentration. The duration time of addition of a batch was 15 min. The temperature of the pulp increased to 90 °C as a result of the heat of the dilution and reaction. This temperature was kept constant with the aid of a silica-coated immersion heater connected to a temperature control unit. After 6 hours the hot slurry was transferred to the three settling tanks (each tank of 200 dm^3 capacity), arranged in cascade system. Two dm^3 of 0.1% flocculant were added to each settling tank while slowly agitating. The settling rate was about 7 cm/min., i.e. after 10 minutes 2/3 of the pulp in the tank became clear from any suspended particles. The clear liquor was decanted in the three tanks. Fresh water was added to the first tank and agitation was continued for 2 min., after which about 400 cm^3 0.1% flocculant were added while gently stirring for about 2 min. The clear liquor was decanted and fed to the second settling tank and the process was repeated in the second and third tanks till the attainment of pH 7 in the third tank which is achieved after 8 decantation steps. The thick slurry containing about 50% of the solid was pumped with a slurry pump to the rotary drum filter to decrease the moisture of the ore to about 25% and then it was dried at 110 °C in the shelf dryer. The obtained product contained MnO_2 84.6%, Fe_2O_3 2.23%, SiO_2 1.98%, Al_2O_3 0.50%, S 0.015%, and P 0.030%. It was noticed from the chemical analysis that R_2O_3 content decreased from 11.5 to 2.7%. The obtained product was tested for the production of welding flux and the results were positive. The suggested flowsheet for the production of pyrolusite with low iron content is shown in Fig. 2.

CONCLUSION

The Fe_2O_3 content in the ore decreased from 10.35% to 2.23% and the MnO_2 content increased from 70% to 84% by leaching with 30% H_2SO_4 at 90 °C for 6 hours at 13% content of the solids. The solids/liquid separation was achieved by

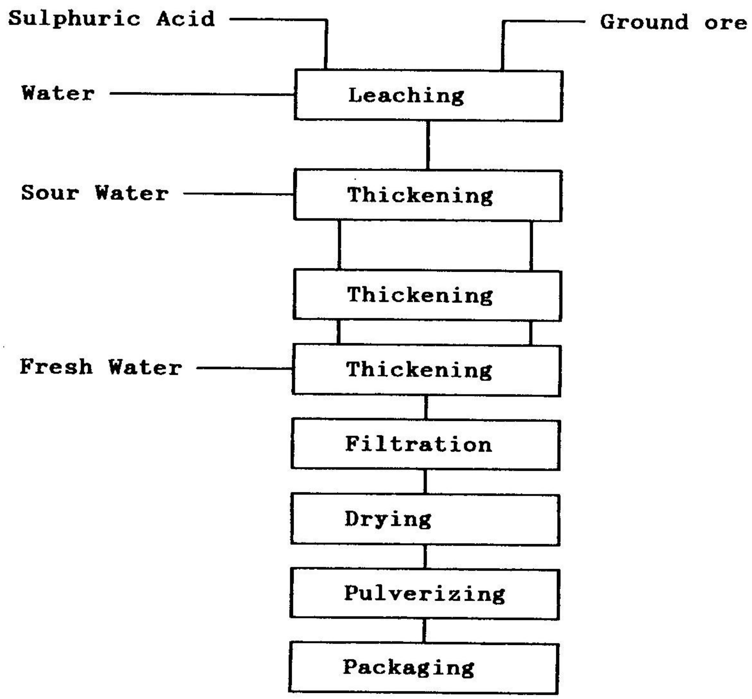

Fig. 2. Block flowsheet for production of pyrolusite sample with low iron cotent

settling and decantation in 8 steps. The product is suitable as a feedstock for welding flux manufacture.

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REFERENCES

SCHWEMMER D.D., JANZER H.E., OLSON D.L. (1978), International Conf. Trends in Steels & Consumables for Welding. The Welding Institution, Paper No. 34 Vol. 1, London 13–16 Nov.

CMRDI (1989), *Beneficiation of a Manganese Ore For Welding Electrodes Production*, Report Presented to Orlicon Co., by CMRDI, Cairo, Egypt.

YOUNG R. S. (1971),*Chemical Analysis in Extractive Metallurgy*, Charles Griffin & Co., Ltd. London.

Ibrahim I.A., Abdel-Aal E.A., El-Safty N.A., Ismail A.K., (1995), Hydrometalurgiczna przeróbka rud manganowych z Synaju, *Fizykochemiczne Problemy Mineralurgii,* 29 73–79, (English text)

Otuliny elektrod spawalniczych zwieraja do 30 % (w przeliczeniu na MnO) rudy manganowej a zawartość żelaza i siarki w rudzie nie może przekraczać 1,7% Fe i 0,02% S. Surowa ruda z Synaju o średniej zawartości manganu, którą użyto w tych badaniach, zawierała około 7% Fe i 0,4% S, nie nadawała się do tego celu. Separacja magnetyczna nie doprowadziła do ekonomicznego usunięcia tych składników z rudy z powodu jej złożonego charakteru. Stwierdzono, że bezpośrednie ługowanie rudy kwasem siarkowym jest efektywną metodą redukcji zawartości żelaza w rudzie manganowej do wymaganego poziomu, a siarka zostaje usunięta przez wielokrotne wymywanie. Przebadano systematycznie proces ługowania rudy i ustalono warunki optymalne procesu. Na podstawie tych wyników przeprowadzono testy na skalę pilotową w reaktorze o pojemności 600 dm^3. Stwierdzono, że ługowanie pozwala na obniżenie zawartości żelaza i siarki do poziomu 1,6% Fe i 0,019% S.