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Recovery of Manganese Using Molasses as Reductant in Nitric Acid Solution

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Abstract

The present work provides an investigation of the recovery of manganese from a relatively low-grade ore (37.5% Mn) located in Um Bogma, Sinai area, Egypt. Several leaching experiments have been performed in HNO_3 acid medium to which molasses as an additive was used to benefit from the reduction action of glucose and fructose. Leaching parameters were optimized as 2.7 M HNO_3 in the presence of molasses (20% of the input weight) in a solid-liquid ratio of 1:12 at 95°C for 2 hrs. Under these conditions, the recovery efficiency of manganese attained about 98%, whilst iron dissolution did not exceed 12.9%. The recovery efficiencies of the interesting associated metal values (Cu, Co, Zn, Ni and Cr) have also been investigated. Manganese oxide was recovered from leach liquor in basic media after removal of major gangue impurities by precipitation technique. High purity manganese oxide products namely, (Bixbyite Mn_2O_3) and activated manganese oxide (hausmannite Mn_3O_4) were prepared. The latter was obtained via precipitation in basic media followed by activation using HNO_3 as oxidant and ignition. The obtained products were suitable for several industrial applications besides, ammonium nitrate as added by product.

Introduction

Manganese plays a key role in the development of various industrial activities such as steel production, dry batteries, dietary additives preparation, fertilizers, fine chemicals and some medicines [1]. The world annual production of the total manganese alloys passed 10.3 million metric tons and it is destined to increase. Exhaustion of relatively rich manganese ores has focused attention on the possible exploitation of its low grade ores. Besides, the low grade manganese ores has also generated a lot of interest as a potential source of associated metal values such as cobalt, nickel, copper, zinc, chromium, vanadium and molybdenum. Therefore, several hydrometallurgical processes have been developed for these ores involving, dissolving manganese as soluble chloride, sulphate or nitrate and subsequently purifying the obtained liquor each by different technologies such as precipitation (as hydroxides, sulphides or basic salts), solvent extraction, electro-winning and adsorption onto activated matrices.

Um Bogma Mn-Fe deposit is located in the marine intercalation within the clastic Paleozoic section at the south west Sinai, Egypt. The ore bodies are generally irregular in shape and tend to be lenticular. In some parts, the ore body is present as different vien fillings cutting through the surrounding dolomite [2]. Many processes have been investigated for the treatment of low grade manganese ores either by reduction roasting followed by acid leaching [3] or directly by reductive acid leaching using different kinds of reducing agent and acids [4]. These include mainly sulphuric acid and hydrogen peroxide [4,5], phenol [6], oxalic acid [3], iron sulphate [7], pyrite [8], aqueous sulphur dioxide [9-11], hydrochloric acid and nickel matte [12], pyrite [13-16], H_2O_2 [17]. Processes in basic media involve essentially the use of ammonium sulphite [18], or ammonium thiosulphate/sulphite [19]. Adopting a zero-waste approach, carbohydrates from agriculture wastes are low-cost, renewable and non hazardous and can be used reducing agent for manganese leaching under mild acidic conditions [20-28].

The aim of this work is to investigate a new leaching process of the relatively low grade manganese ore from Um-Bogma locality by nitric acid in presence of molasses as reductant. This method would

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provide low iron dissolution during the leaching process as well as it would decrease the leaching efficiency of the associated metal values. Molasses, as obtained from conventional sugar extraction procedures, are essentially composed of glucose and fructose together with some residual sucrose in varying proportions depending upon the source. In case of sugar cane, the produced molasses may contain glucose, fructose and sucrose. While both glucose and fructose are reducing agents, sucrose is not because both anomeric carbons are involved in acetal formation, it can be inverted to glucose and fructose according to the following reaction:

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{11}O_6 \quad (1)$$

Glucose and fructose would indeed reduce MnO_2 in its ores according to the following reaction [18,19]:

$$C_6H_{12}O_6 + 12\ MnO_2 + 24H^+ \rightarrow$$

$$\rightarrow 6CO_2 + 12Mn^{+2} + 18H_2O \quad (2)$$

In particular, molasses used as a reducing agent undergoes a series of degradation reaction giving different organic compounds able to complex ions in solutions and then increasing their solubility [29].

Experimental

Characterization of the Manganese Ore

The working manganese ore sample was collected from Um-Bogma area which is located in west central Sinai, Egypt. The ore sample was first crushed to +60 mesh (+250 μm) and then ground to the required particle size of (–74 μm). To define the mineralogical composition of the collected manganese ore both bulk and sieved samples were subjected to X-ray diffraction (XRD) analysis. Sample characterization by XRD showed the presence of variety of manganese minerals mainly pyrolusite, cryptomelane, hetaerolite and jacobsite. The presence of iron minerals like goethite and hematite were also observed, as well as dolomite. From the obtained analytical and mineralogical results, the following potential mineralogical composition of the working Um-Bogma low grade Mn ore is given in Table 1. In the latter, certain assumptions have been taken in consideration. Thus the total iron is assumed to be mostly hematite while goethite is of minor importance. This has been deduced from the corresponding ignition loss of about 1.42% as H_2O^+. In the mean time, all the present CaO (6.50%) has been calculated as dolomite (21.31). the analyzed Mn has however, been included as MnO due to its presence in mixed oxide states.

Table 1
Potential mineralogical composition of studied ore

Mineral/Oxide	wt.%
Quartz/silicate*	11.68%
Dolomite	21.31%
Iron oxide minerals**	17.00%
Manganese minerals	46.11% (equivalent MnO)
ZnO	1.50%
Total	97.60%

*Silicates are mostly clay
**Involved mainly hematite and minor geothite

Analytical Procedures

The ore was analysed for its major, minor and trace elements using the proper analytical methods [30,31] as shown in Tables 2 and 3. Total iron was titrimetrically determined against EDTA using sulfosalicylic acid while the ferrous content was analyzed titrimetrically against standard potassium dichromate. The spectrophotometric determination of titanium content was performed at 430 nm using tiron as complexing agent (Unicam UV2-100). Both calcium and magnesium were titrimetrically determined against EDTA using murexide and Eriochrome Black T indicators. The molybdate reagent in the presence of tartaric acid has been used for determination of the silica content. Aluminum was analyzed colorimetricly using alizerine red as indicator. Analysis of the trace elements present was performed by means of an atomic absorption (Unicam 969 Model).

Leaching Procedure

The performed leaching tests were carried out to which varying amounts of molasses were added using 10 g sample portions of ore and 120 ml of HNO_3 in closed glass flasks. The obtained ore slurry was then agitated at the required temperature using a hot magnetic plate for a specified reaction time. At the end of each leaching experiment, the slurry was filtered and the filtrate (leach liquor) was analysis for leached manganese and other associated metal values.

Table 2
Chemical composition of major and minor elements of Um-Bogma studied ore

Component	wt.%
SiO_2	9.91%
TiO_2	0.21%
Al_2O_3	1.25%
Fe_2O_3	17.00%
MnO	46.11%
MgO	05.01%
CaO	06.50%
Na_2O	0.21%
K_2O	0.31%
P_2O_5	0.11%
LOI*	11.63%
Total	98.25%

*Loss on ignition at 1000°C

Table 3
Trace elements composition of Um-Bogma studied ore

Component	Concentration, ppm
Zn	15000
Cu	267
Co	115
Ni	411
Cr	407

Results and Discussion

Leaching Results

Effect of Acid Concentration

The effect of HNO_3 acid concentration between 0.5 and 3.5 M on the reductive leaching of Um-Bogma manganese ore in the presence of molasses is illustrated in Fig. 1. The other leaching conditions were fixed at 100°C for 3 hrs, in presence of molasses (20% of the input sample weight) and using ore sample ground to 74 μm grain size. From the obtained results, it was shown that recovery of manganese sharply increased from 29.22% to 99.9% when using 0.45 M to 3.38 M HNO_3. Recovery of Cu, Zn and Co exhibits a relatively sharp increase by increasing the acidity from 0.45 M to 1.8 M after which a slight increase has been observed. However, Cr and Ni in particular have only exhibited a low rate of recovery. At 2.7 M acidity, the dissolved iron content did not exceed 13%. Those relatively low efficiencies are most probably due to decreased acid strength due to reaction with the manganese minerals and dolomite beside molasses. In addition, the possible reduction of some of these metallic associates in this complex medium into their less soluble reduced species might occur. Alternatively, the decreased solubility of the associated metal values might be due to their presence in some minute refractory mineral forms. By increasing the HNO_3 concentration to 3.38 M, Mn recovery has attained 99.9% while that of iron amounted 18.5%. Therefore, it can be mentioned that a concentration of 2.7 M HNO_3 would be sufficient for almost complete recovery of manganese while keeping minimum iron dissolution.

It is interested in this regard to mention that calculation of the acid requirement (stoichiometric) for manganese dissolution according to reaction (2) in which all Mn is assumed to be present as MnO_2 revealed that 1 ton ore necessitated about 0.90 ton HNO_3. To the latter, about 0.3 ton acid would be required for dissolution of the present dolomite 21.35% according to the following reaction:

$$(Ca,Mg)O + 2HNO_3 \rightarrow$$
$$\rightarrow (Ca,Mg)(NO_3)_2 + H_2O \qquad (3)$$

The chosen 2.7 M HNO_3 in a solid/liquid ratio of 1:12 indicate that the input acid is equivalent to about

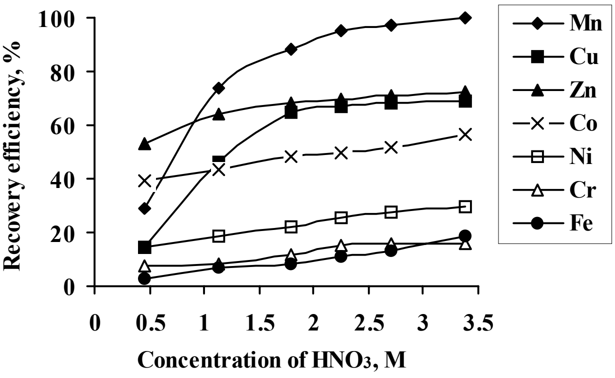

Fig. 1. Effect of HNO_3 acid concentration upon the recovery efficiencies of Mn and associated metal values from Um-Bogma ore (20% stoichiometric of molasses, 1:12 pulp density, 100°C, 3 hrs).

2 ton per 1 ton ore. The optimized conditions determined in an Italian pyrolusite ore [20,21] and using sequential factorial design and evaluating the statistical significance of the different factors by analysis of variance (ANOVA) involved indeed stoichiometric HNO_3 acid together with less than 20% of the calculated stoichiometric glucose amount and using ore grain size of 295-417 µm.

Effect of Molasses Amount

In order to evaluate the effect of molasses addition upon the manganese reduction, a series of leaching experiments were carried out using 2.7 M HNO_3. These experiments were performed in the absence and presence of different amounts of molasses varying from 10% to 40% of the input sample weight. The other leaching conditions were fixed at a solid/liquid ratio of 1:12 at 100°C for 3 hrs and using –74 µm for ore grain size. From the obtained data as shown in Fig. 2, it is evident that while only about 10.76% of input Mn has been dissolved in the absence of molasses, the leaching efficiency of the associated metal values were lowered to 46.72% Zn, 52.32% Cu, 20.26% Co, 13.16% Ni and 3.55% Cr. These data reveal that these metal values might be at least partially incorporated in the Mn minerals. Thus the reduction of manganese in its minerals to its bivalent state is a pre-requisit for its dissolution as mentioned above. On the other hand, increase the molasses amount beyond 20% of the input sample weight has a pronounced effect upon iron dissolution which increased from 12.9% to 31% at 40% of the input sample weight of molasses.

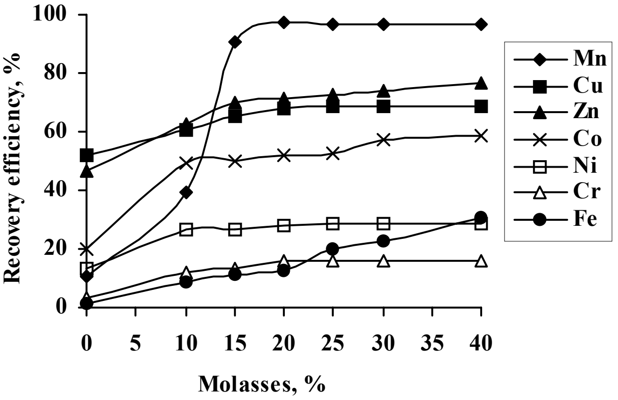

Fig. 2. Effect of molasses addition upon the recovery efficiencies of Mn and associated metal values from Um-Bogma ore (2.7 M HNO_3, 1:12 pulp density, 100°C, 3 hrs).

Effect of Time

In a trial to improve the leaching conditions, another experimental leaching series was performed using < 2 hrs leaching time. In these experiments, the leaching conditions were kept fixed; namely, 2.7 M HNO_3 in the presence of molasses (20% of the input sample weight) at 100°C in a solid/liquid ratio of 1:12. From the results shown in Fig. 3, it was ascertained that at only half an hour leaching time, the obtained recovery efficiencies of Mn lowered to 76.57%, 61.8% for Cu, 46.04% for Zn, 47.08% for Co, 24.30% for Ni, 10.49% for Cr and iron down to only 5.7%. Whilst after 1 hour the recovery efficiencies of Mn sharply increased to reach 94.36% and after 90 minute it was slightly increase giving 97.1%. Therefore, it can be concluded that 1.5 to 2 hrs leaching time would be adequate and considered as optimum.

Effect of Temperature

In order to reduce the heat energy and in turn of the leaching costs, four leaching experiments were carried out at room, 50, 75, 85 and 95°C under the same conditions previously used at 100°C. The resultant recovery efficiencies as shown in Fig. 4 indicate that the temperature plays a critical role in leaching Mn and the associated metal values. For example, working at room temperature the obtained recovery yield for Mn and Cu was decreased down to only 51.6% and 34.88% as compared to 97.27% and 68.32% at 95°C respectively.

Effect of Pulp Density

Working with the fixed concentration of 2.7 M HNO_3 in presence of molasses (20% of the input

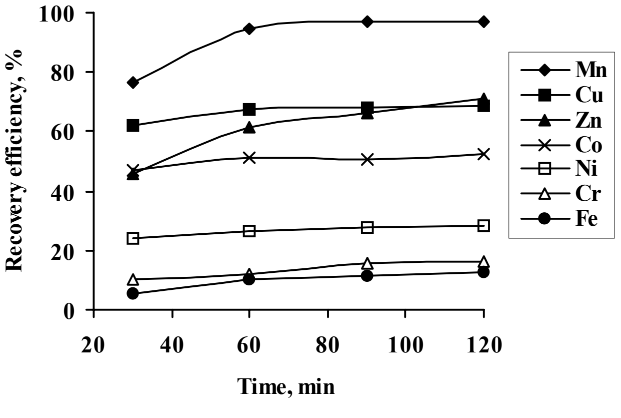

Fig. 3. Effect of time upon the recovery efficiencies of Mn and associated metal values from Um-Bogma ore (2.7 M HNO_3, 20% stoichiometric of molasses, 1:12 pulp density, 100°C).

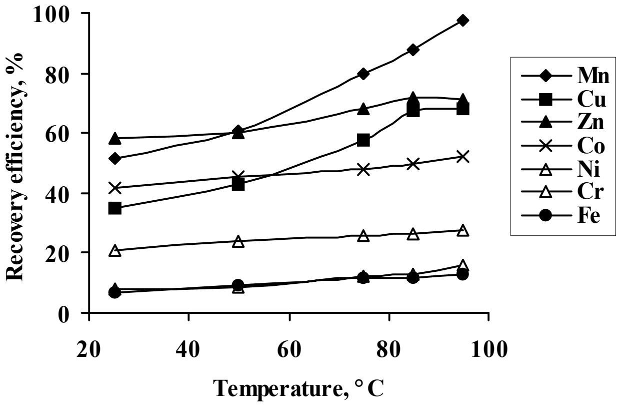

Fig. 4. Effect of temperature upon the recovery efficiencies of Mn and associated metal values from Um-Bogma ore (2.7 M HNO_3, 20% stoichiometric of molasses, 1:12 pulp density, 2 hrs).

sample weight), another three leaching experiments were performed using the pulp densities 1:8, 1:10 and 1:15 for 2 hrs and at 95°C. In these experiments, the total acid input would thus be according to variation in the input wt./vol. ratio. From the obtained results shown in Fig. 5, it was found that when using 1:8 and 1:10 pulp ratios, the recovery efficiencies of all the studied metal values have been lowered however, in varying degrees. Increasing the acid amount by applying the pulp ratio of 1:15 did not however, being about any perceptible improvement in the recovery efficiency of Mn, Cu, Ni, Co, Cr and Zn but increased the iron dissolution to 19%.

Recovery of Manganese Product

To eliminate the concomitant elements released in the leach liquor, precipitation technique was employed. Complete iron precipitation as Fe_2O_3 and other impurities was achieved by using ammonium hydroxide at a pH value of 7. After filtration, the manganese value left behind in the filtrate by precipitation at pH 9 using sodium hydroxide. The obtained product was then ignited 1000°C for 1 hour and was found to be is a typical (Bixbyite Mn_2O_3) as indicated by XRD analysis, [card No. 10-69], Fig. 6.

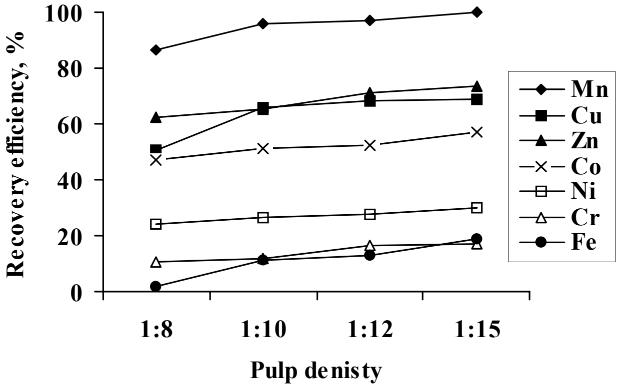

Fig. 5. Effect of pulp density upon the recovery efficiencies of Mn and associated metal values from Um-Bogma ore (2.7 M HNO_3, 20% stoichiometric of molasses, 2 hrs, 95°C).

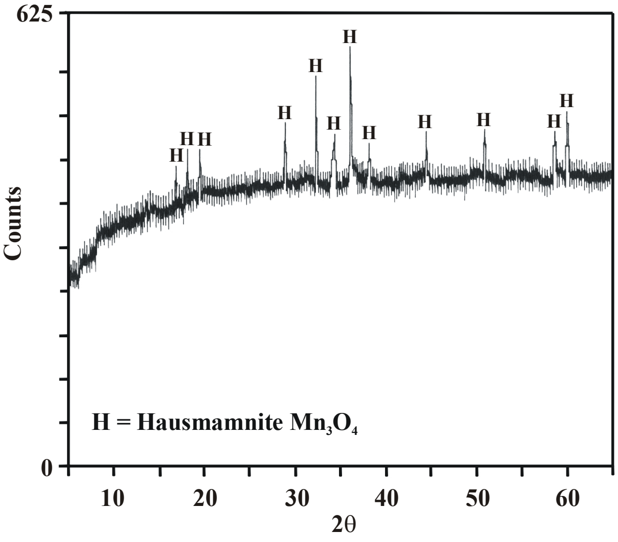

Fig. 6. XRD analysis of manganese product without treatment with nitric acid.

On the other hand, it has also been possible to activate the activated hydroxide using HNO_3 as oxidant [32] and baking at 200°C. A typical hausmannite (Mn_3O_4) product was thus obtained after ignition at 1000°C as recorded by XRD analysis, [card No. 1-1127], Fig. 7.

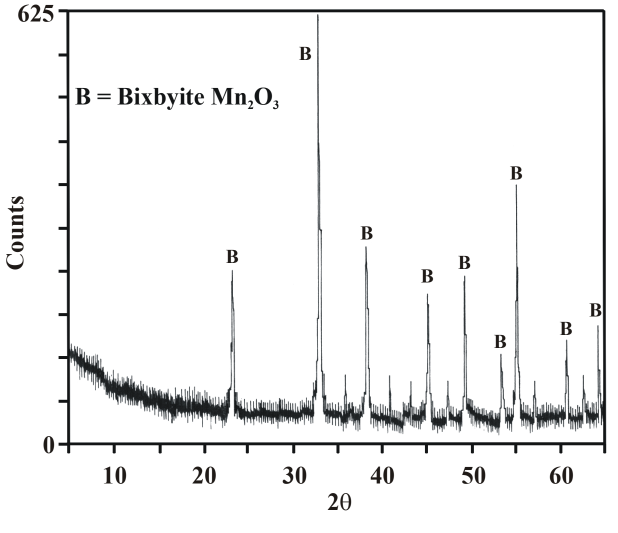

Fig. 7. XRD analysis of manganese product with treatment with nitric acid.

The chemical analysis of the latter product was found to attain in a purity of 99.95%. In the latter, only Zn was found as impurity (120 ppm). The SEM micrograph and EDX of the latter are depicted in Fig. 8. Two peaks in the Fig. 8 were related to K and L shells of manganese atom. The block diagram of the suggested hydrometallurgical process is given in Fig. 9. Residual nitric acid from the activation step could be recycled and reused. Also, NH_4NO_3 can be recovered as a secondary useful product which is used as a fertilizer.

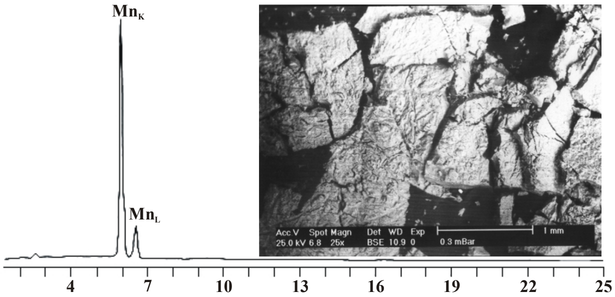

Fig. 8. SEM analysis of the highly concentrated and pure manganese product.

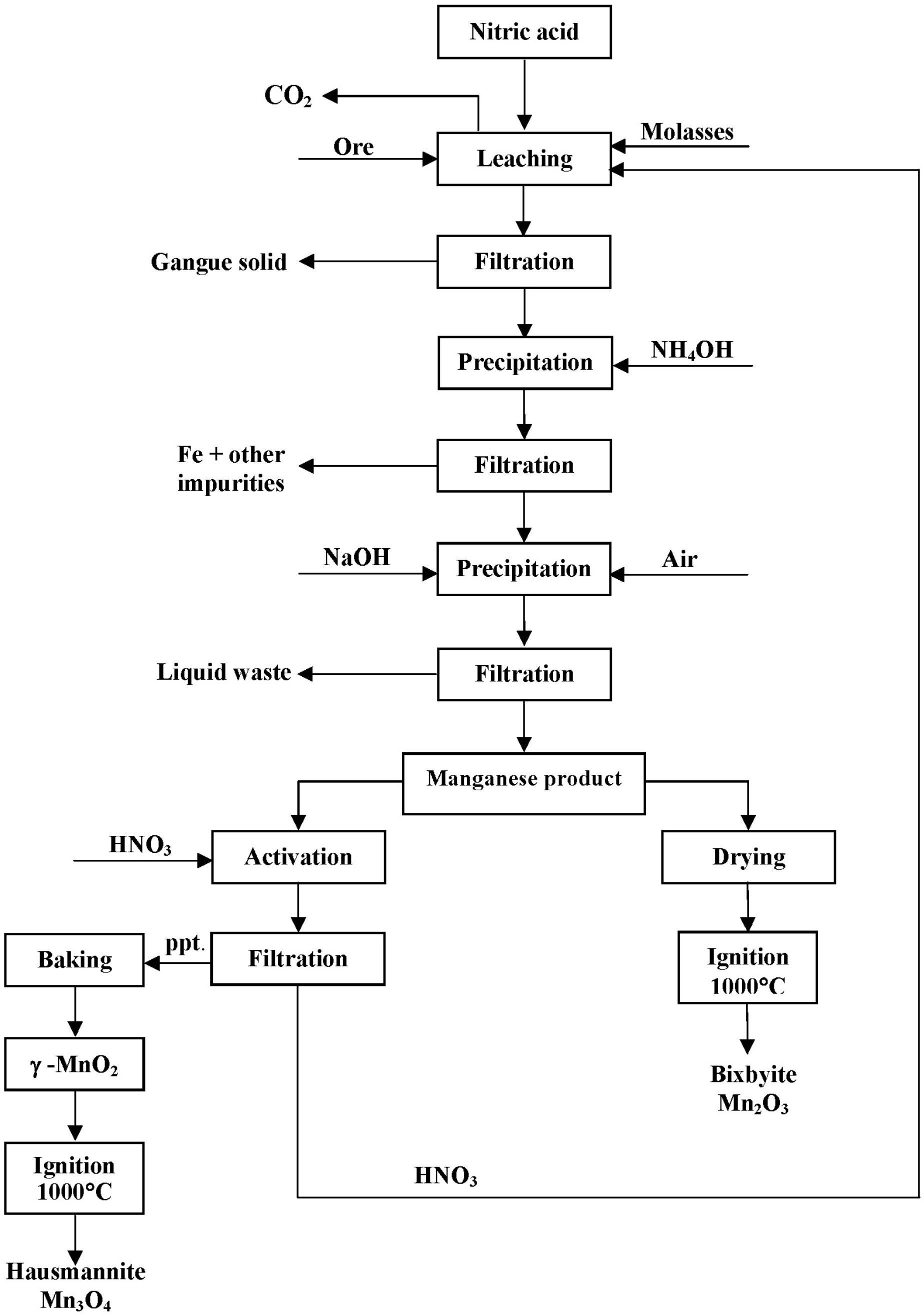

Fig. 9. Block diagram for the hydrometallurgical production of activated and non activated manganese products.

Conclusions

In this work, high-purity manganese oxides were obtained from acid reductive leaching of a relatively low grade Sinai manganese ore using a proper molarity of nitric acid in presence of molasses as the reducing agent. In this proposed method, the other associated metal values have also been leached in varying efficiencies; namely Zn, Cu, Co, Ni and Cr. The studied relevant leaching factors were optimized as 2.7 M HNO_3 in presence of molasses (20% of the input sample weight), 95°C in a solid/liquid ratio of 1:12 for 1.5 to 2 hrs leaching time and using an ore ground to –74 μm grain size. Using this relatively low leaching time is justified by decreased energy consumption. Under these conditions the leaching efficiency of manganese attained about 98% together with 68.32% for Cu, 71.39% for Zn, 52.40% for Co besides relatively low results of 27.80% for Ni and 16.19% for Cr. On the other hand, the iron dissolution was as low as 12.9%. Environmentally, this leaching process can be considered friendly where the possibility of using molasses (industrial wastes) as a non-hazardous waste material has been realized. Moreover, exhausted solids can be made inert and re-used in building-block production according to a zero approach. For the recovery of the dissolved manganese value, a precipitation technique has actually been applied and two products have been prepared. In the first, bixbite (Mn_2O_3) was prepared by stepwise precipitating the co-dissolved impurities at pH 7 followed by precipitation of manganese at pH 9 using NaOH and air as oxidant followed by ignition at 1000°C. The second product was prepared by activation of the precipitated manganese using HNO_3 and baking at 200°C to obtain γ-MnO_2 while can be followed by ignition at 1000°C to obtain hausmannite (Mn_3O_4).

References

1. Sahoo, R.N., Naik, P.K., Das, S.C., Hydrometallurgy, 62:157 (2001).
2. EL-Gammal R.M.H., 1984. Geological studies on the Stratigraphic Succession of Um-Bogma District, West-Central Sinai, M. SC. Thesis, Cairo University, Egypt.
3. Sahoo, R.N., Srinivasa, R.K., Int. J. Miner. Process, 25 (1-2):147 (1989).
4. Tao Jiang, Yongbin Yang, *et al.*, Hydrometallurgy, 69, 177 (2003).
5. Tao Jiang, Yongbin Yang, *et al.*, Hydrometallurgy, 72:129 (2004).
6. Qiliu, Y.Z, Sun, C. Minerals Engineering, 14 (5): 525 (2001).
7. Das, S.C., Sahoo, P.K., Rao, P.K.., Hydrometallurgy, 8:35 (1982).
8. Amer, A.M., Fizyko chemiczne problemy metalurgii, 32:195 (1998).
9. Abbruzzese, C., Hydrometallurgy, 25 (1):85 (1990).
10. Abbruzzese, C., Duarte, M.Y., Paponetti, B., Toro, L., Miner. Eng, 3 (3-4):307 (1990).
11. Vegliò, F., Toro, L., Hydrometallurgy, 36:215 (1994).
12. Chen, H.-H., C. Fu, D.-J. Zheng, Hydrometallurgy, 28:269 (1992).
13. Kanungo, S.B., Hydrometallurgy, 52:331 (1999).
14. Kanungo, S.B., Hydrometallurgy, 52:313 (1999).
15. Kanungo, S.B., Jena, P.K., Hydrometallurgy, 21: 23 (1988).
16. Kanungo, S.B., Jena, P.K., Hydrometallurgy, 21: 41 (1988).
17. El Hazek, M.N, Lasheen, T.A.I, Helal, A.S., Hydrometallurgy, 84 (Issues 3-4):187 (2006).
18. Das, R.P., Anand, S., Das, S.C., Jena, P.K., Hydrometallurgy, 16:335 (1986).
19. Niinae, M., Komatsu, N., Nakahiro, Y., Wakamatsu, T., Shibata, J., Hydrometallurgy, 40:111 (1996).
20. Pagnanelli, F., Furlani, G., Valentini, P., Vegliò, F., Toro, L., Hydrometallurgy, 75:157 (2004).
21. Pagnanelli, F., Garavini, M., Vegliò, F., Toro, L., Hydrometallurgy, 71:319 (2004).
22. Trifoni, M., Vegliò, F., Taglieri, G., Toro, L., Miner. Eng, 13:217 (2000).
23. Trifoni, M., Toro, L., Vegliò, F., Hydrometallurgy, 59 (1):1 (2001).
24. Vegliò, F., Toro, L., Int. J. Min. Process, 40:257 (1994).
25. Vegliò, F., Trifoni, M., Abbruzzese, C., Toro, L., Hydrometallurgy, 59 (1):31 (2001).
26. Volpe, I., Trifoni, M., Toro, L., Ind. Eng. Chem. Res, 39 (8):2947 (2000).
27. Vegliò, F., Trifoni, M., Toro, L., Ind. End. Chem. Res, 40 (18):3895 (2001).
28. Furlani, G, Pagnanelli, F, Toro, L., Hydrometallurgy, 81 (Issues 3-4) 234 (2006).
29. Fagan, R.D., Grethlein, H.E., Converse, A.O., Porteous, A., Environ. Sci. Technol, 5 (6):545 (1971).
30. Marczenko, Z., Spectrophotometric Determination of Elements, John Wiley and Sons, New York., 1986.
31. Welz, B., Sperling, M., Atomic Absorption Spectrometry, 3-rd Ed., Wiley-VCH Weinheim, New York, 1999.
32. Kuz'miniskii, Ye.V., Andriiko, A.A., Nyrkova, L.I., J. Power sources, 52:49 (1994).

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