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Modeling and Optimization of Reductive Leaching Of Manganese from Low-Grade Manganese Ore in H_2SO_4 Using Glucose as Reductant

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Abstract
Leaching studies of low-grade Egyptian manganese ore containing 25.3% MnO_2, and 52.06 % Fe_2O_3 using glucose as reductant in sulfuric acid medium. The experiments were designed according to 2^5 full factorial design, and regression equation for the extraction of Mn was determined as a function of H_2SO_4 concentration (C), H_2SO_4/Mn stoichiometric (S), glucose/Mn mole ratio (G), leaching temperature (T), and leaching time (M). The main factors affecting Mn dissolution are X_1 (C), and X_4 (T) that are the most positive significant. While the interaction of X_1X_4 (C : T), X_1X_5 (C : M), X_2X_3 (S : G), $X_1X_2X_3$ (C : S : G) $X_1X_3X_5$ (C : G : M) are positive significant which mean that the increase in these variables increasing the Mn recovery. On the other hand, the interaction between $X_2X_3X_4$ (S : G : T), and $X_2X_4X_5$ (S : T : M) are negatively significant, which means that increasing these effects decreasing the Mn recovery.
Key words: *Mn ore, leaching, glucose, reductant, Mn recovery, factorial design.*

I. INTRODUCTION

Manganese is a strategically important metal that has several industrial uses. The most important are in the manufacture of steel, some non-ferrous alloys, carbon-zinc batteries and some chemical reagents.

Manganese ore, present in the form of Pyrolusite (MnO_2), occurs at various localities in Egypt with reserves amounting more than 401 million tons. The dissolution of manganese dioxide in an acid media is very difficult. While, dissolution in an acid media in the presence of reducing agent is a well known hydrometallurgical process. Many kinds of reductant (oxalic acid, corncob, cornstalk, cane molasses, Organic Alcohols and so on) have been successfully employed [1-5].

The ability of alcohols to decrease metal oxidation state is well reported in the literature [5-8], but little information regarding the effect of mixed reaction media on the metal ion solubility is available.
The manganese sulfate produced is a chemical product particularly employed in the fertilizer production and in zoo-technical field as additive in animal feed. Therefore, the investigation of new nontoxic and environmentally friendly hydrometallurgical process for the manganese dioxide dissolution is the acid extraction performed by a carbohydrates as a reducing agent. The stoichiometric and kinetic aspects concerning the chemical dissolution are shown elsewhere [9, 10]. The overall chemical reaction, which takes place during the manganese dioxide leaching by using glucose and sulfuric acid, is shown below:

$C_6H_{12}O_6$+12 MnO_2+24 H^+ 6CO_2+12 Mn^{2} $\xrightarrow{+\ \ +}$ 18 H_2O ……(1)

During this reaction several metals present in the mineral (such as calcium, iron, aluminum and so on) are dissolved. In spite of the high selectivity of the MnO_2 reduction, some purification steps are therefore necessary.

The aim of the present work is to study the influence of glucose as reductant on the dissolution of MnO_2 from Om-Bogama, Egypt, low grade ore in sulfuric acid. The experiments have been carried out using a statistical design.

II. EXPERMENTAL

Source and analysis of manganese ore:

The sample of low grade manganese ore employed in this study from Om-Bogama, Sinai, Egypt, was supplied by the mineralogical and Geological Research Institute, Cairo. The collected sample was ground to below 150 μm and sieved using a 105μm sieve.

One gram of ore was digested in aqua regia and filtered with Whatman No. 542 (ash less) filter paper. The filtrate was analyzed for the different elements using Pereken Elmer atomic absorption. Chemical analysis of the ore is given in Table I.

Dissolution tests

The factorial experiments were conducted using near mono-size (-150+105 µm) particles to reduce the effect of size.

A 250ml flask was taken. One hundred milliliters of sulfuric acid solution and glucose of required amount was poured in to it. The flask was then mechanically stirred and heated in a thermo-stated water bath. When the solution attained the pre-required temperature, the pre-calculated weight of ore was added. The rate of agitation was kept constant for all the experiments. After each experiment, the slurry was filtered and the residue was washed with double-distilled water. The leach liquor along with wash was analyzed for Mn using AAS.

Experimental planning

In the present work, 2^5 full factorial design was chosen for conducting the leaching experiments [11]. The experiments were carried out under the variables selected sulfuric acid concentration (C), sulfuric acid stoichiometric (S), manganese to glucose mole ratio (G), leaching time (M) and leaching temperature (T). The levels of variables are given in Table II.

III. RESULT AND DISCUSSION

The coded variables for 2^5 full factorial design and the results showing recovery of Mn is given in Table III. The regression equation for the above matrix may be represented as follow:

$$Y= b_o +b_1X_1 + b_2X_2 + b_3X_3 + b_4X_4 + b_5X_5 + b_{12}X_1X_2 + b_{13}X_1X_3 + b_{14}X_1X_4 + b_{15}X_1X_5 + b_{23}X_2X_3 + b_{24}X_2X_4+ b_{25}X_2X_5 + b_{34}X_3X_4 + b_{35}X_3X_5 + b_{45}X_4X_5 + b_{123}X_1X_2X_3 + b_{124}X_1X_2X_4 + b_{125}X_1X_2X_5 + b_{134}X_1X_3X_4 + b_{135}X_1X_3X_5 + b_{145}X_1X_4X_5 + b_{234}X_2X_3X_4 + b_{235}X_2X_3X_5 + b_{245}X_2X_4X_5 + b_{345}X_3X_4X_5 + b_{1234}X_1X_2X_3X_4 + b_{1235}X_1X_2X_3X_5 + b_{1245}X_1X_2X_4X_5 + b_{1345}X_1X_3X_4X_5 + b_{2345}X_2X_3X_4X_5 + b_{12345}X_1X_2X_3X_4X_5 \quad (2)$$

Where Y = the percentage of metal extracted; b= empirical model coefficients; X_1, X_2, X_3, X_4 and X_5 = dimensionless coded factors for sulfuric acid concentration (C) and stoichiometric (S), Mn/glucose mole ratio (G), temperature (T), and time (M), respectively. The relations between the coded and actual values are given as:

$$X_1 = \frac{C - Cm}{\Delta C}, \qquad X_2 = \frac{S - Sm}{\Delta S}, \qquad X_3 = \frac{G - Gm}{\Delta G}$$

$$X_4 = \frac{T - Tm}{\Delta T}, \qquad X_5 = \frac{M - Mm}{\Delta M}$$

Where

$$Cm = \frac{C_+ + C_-}{2}, \qquad \Delta C = \frac{C_+ - C_-}{2}$$

$$Sm = \frac{S_+ + S_-}{2}, \qquad \Delta S = \frac{S_+ - S_-}{2}$$

$$Tm = \frac{T_+ + T_-}{2}, \qquad \Delta T = \frac{T_+ - T_-}{2}$$

And so on for all variables. Where C_+ is the high level and C_- is the low level given in Table II. Therefore:

$$X_1 = \frac{C - 15}{5}, \qquad X_2 = \frac{S - 1.75}{0.25}, \qquad X_3 = \frac{G - 0.375}{0.125}$$

$$X_4 = \frac{T - 75}{15}, \qquad X_5 = \frac{M - 90}{30}$$

The regression coefficients were estimated by:

$$b_o = \frac{\sum Y_i}{N} \quad \& \quad b_j = \frac{\sum X_j Y_i}{N} \quad \& \quad b_{nj} = \frac{\sum (X_{ni} X_{ji}) Y_i}{N}$$

Where X_j, X_{ni} and X_{ji} are the coded singes (+ or -), Y_i is the Mn recovery percentage, and N is the number of experiments (=32).

The regression equation for extraction of Mn was developed and the main interaction coefficients were tested for significance by Student's t –test method at 95 % confidence level. The regression equation (2) becomes:

$Y= 41.24031 +10.99X_1 + 1.57X_2 + 1.12X_3 + 2.12X_4 - 0.78X_5 - 1.32X_1X_2 -0.59X_1X_3 + 6.46X_1X_4 + 3.11X_1X_5 + 4.12X_2X_3 + 1.70X_2X_4 - 1.89X_2X_5 + 0.723X_3X_4 - 0.409X_3X_5 + 0.466X_4X_5 + 9.07X_1X_2X_3 + 0.749X_1X_2X_4 -0.67X_1X_2X_5 - 0.99X_1X_3X_4 + 5.24X_1X_3X_5 + 1.20X_1X_4X_5 - 2.02X_2X_3X_4 - 1.73X_2X_3X_5 - 2.55X_2X_4X_5 - 1.36X_3X_4X_5 + 4.35X_1X_2X_3X_4 + 0.61X_1X_2X_3X_5 + 5.21X_1X_2X_4X_5 + 1.66X_1X_3X_4X_5 - 0.37X_2X_3X_4X_5 - 1.19X_1X_2X_3X_4X_5$ (3)

It is clear from this equation that the main factors affecting Mn dissolution are X_1 (C), and X_4 (T) that are the most positive significant. While the interaction of X_1X_4 (C : T), X_1X_5 (C : M), X_2X_3 (S : G), $X_1X_2X_3$ (C : S : G) $X_1X_3X_5$ (C : G : M) are positive significant which mean that the increase in these variables increasing the Mn recovery. On the other hand, the interaction between $X_2X_3X_4$ (S : G : T), and $X_2X_4X_5$ (S : T : M) are negatively significant, which means that increasing these effects decreasing the Mn recovery.

Using equation (3) the predicted profiles are calculated at the variables were constant as follow sulfuric acid concentration (C = 20 %), sulfuric acid stoichiometric (S = 2), manganese to glucose mole ratio (G = 0.5), leaching time (M = 120) and leaching temperature (T = 90 ^oC), unless otherwise noted. These profiles are shown in Figs 1-10.

These figures reveal the behavior of Mn dissolution from Egyptian manganese ore under different conditions.

IV. CONCLUSION

Full 2^5 factorial study of manganese dissolution using sulfuric acid in the presence of glucose as reductant. It is clear from the above results that The main factors affecting Mn dissolution are X_1 (C), and X_4 (T) that are the most positive significant. While the interaction of X_1X_4 (C : T), X_1X_5 (C : M), X_2X_3 (S : G), $X_1X_2X_3$ (C : S : G) $X_1X_3X_5$ (C : G : M) are positive significant which mean that the increase in these variables increasing the Mn recovery. On the other hand, the interaction between $X_2X_3X_4$ (S : G : T), and $X_2X_4X_5$ (S : T : M) are negatively significant, which means that increasing these effects decreasing the Mn recovery.

V. Acknowledgment

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TABLES

TABLE I: CHEMICAL ANALYSIS OF LOW GRADE MANGANESE EGYPTIAN ORE (-50+105 μm)

Element	Wt%
Fe_2O_3	52.06
MnO_2	25.31
SiO_2	4.72
Al_2O_3	2.71
CaO	1.89
MgO	0.86
BaO	0.53
S	0.84
K_2O	0.28
H_2O	0.39
Loss on Ignition (1000 ^oC)	10.42

TABLE II: THE 2^5 FACTORIAL DESIGN FOR MANGANESE LEACHING: SIZE OF ORE (-150+105 μm).

Variables	**Low level**	**High level**
X_1 H_2SO_4 Conc., wt% (C)	10.0	20
X_2 H_2SO_4 Stoich. (S)	1.50	2.0
X_3 Mn/G mole ratio (G)	0.25	0.5
X_4 Temperature, ^oC (T)	60.0	90
X_5 Leaching time, min (M)	60.0	120

TABLE III: RESULTS OF 2^5 FULL FACTORIAL EXPERIMENTS

No.	X_1	X_2	X_3	X_4	X_5	Y (Mn recovery, %)
1	-	-	-	-	-	12.13
2	+	-	-	-	-	22.68
3	-	+	-	-	-	12.53
4	+	+	-	-	-	29.29
5	-	-	+	-	-	19.70
6	+	-	+	-	-	28.14
7	-	+	+	-	-	25.13
8	+	+	+	-	-	35.56
9	-	-	-	+	-	32.81
10	+	-	-	+	-	67.27
11	-	+	-	+	-	34.70
12	+	+	-	+	-	70.86
13	-	-	+	+	-	22.48
14	+	-	+	+	-	34.07
15	-	+	+	+	-	15.83
16	+	+	+	+	-	51.45
17	-	-	-	-	+	34.81
18	+	-	-	-	+	59.93
19	-	+	-	-	+	25.96
20	+	+	-	-	+	48.74
21	-	-	+	-	+	48.78
22	+	-	+	-	+	72.43

23	-	+	+	-	+	36.06
24	+	+	+	-	+	44.56
25	-	-	-	+	+	24.83
26	+	-	-	+	+	35.23
27	-	+	-	+	+	40.86
28	+	+	-	+	+	73.24
29	-	-	+	+	+	42.76
30	+	-	+	+	+	76.56
31	-	+	+	+	+	54.48
32	+	+	+	+	+	85.83

Where (-) : low level ; (+) : high level

FIGUERS
FIGURFIGURES

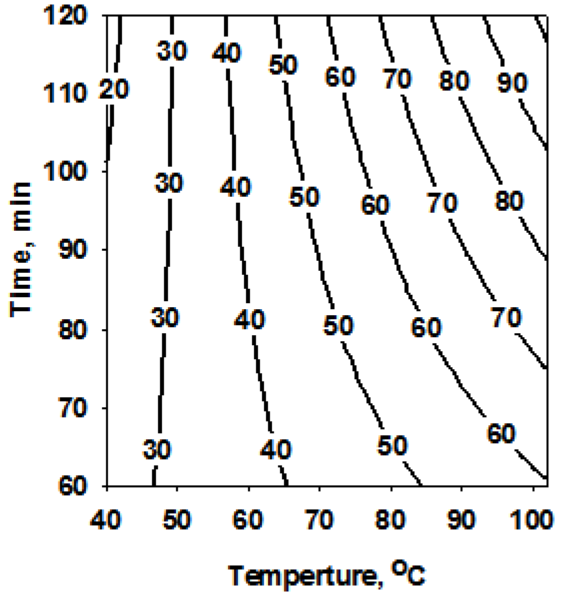

Fig. 1: The Effect of Time and Temperature on Mn Recovery %

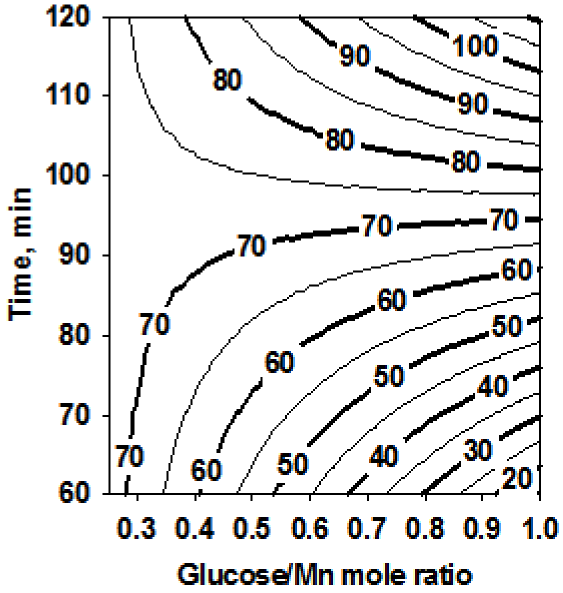

Fig. 2: The Effect of Time and G/Mn Mole Ratio on Mn Recovery %

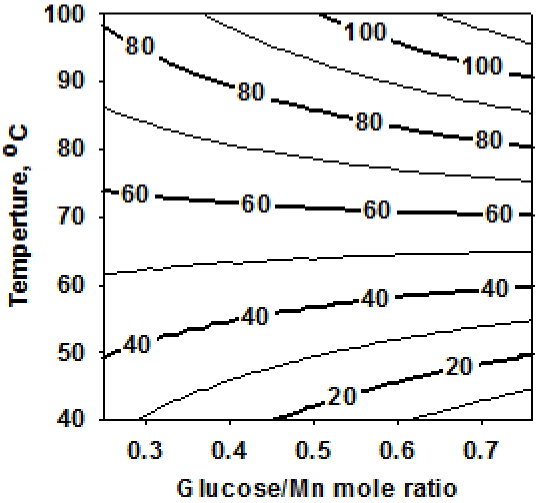

Fig. 3: The Effect of G/Mn Mole Ratio and Temperature on Mn Recovery %

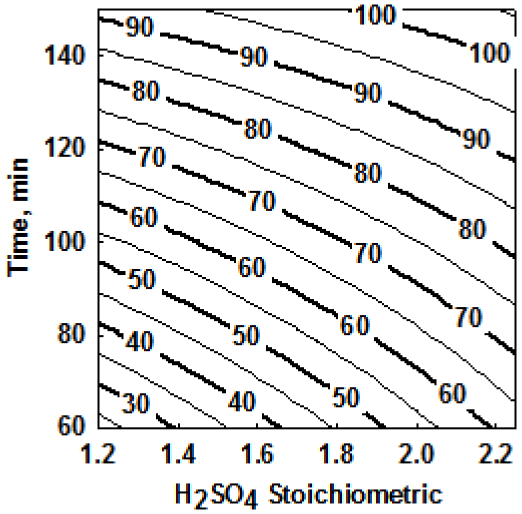

Fig. 4: The Effect of Time and H_2SO_4 Stoich. on Mn Recovery %

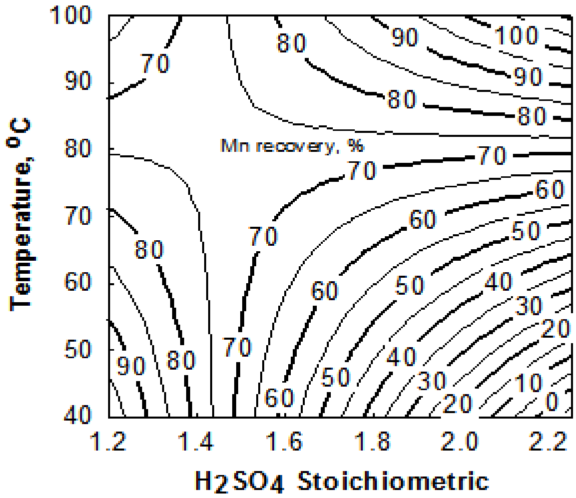

Fig. 5: The Effect of H_2SO_4 Stoich. and Temperature on Mn Recovery %

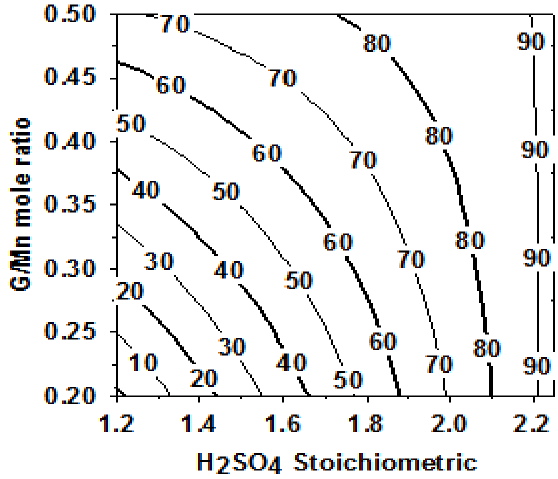

Fig. 6: The Effect of H_2SO_4 Stoich. and G/Mn Mol Ratio on Mn Recovery %

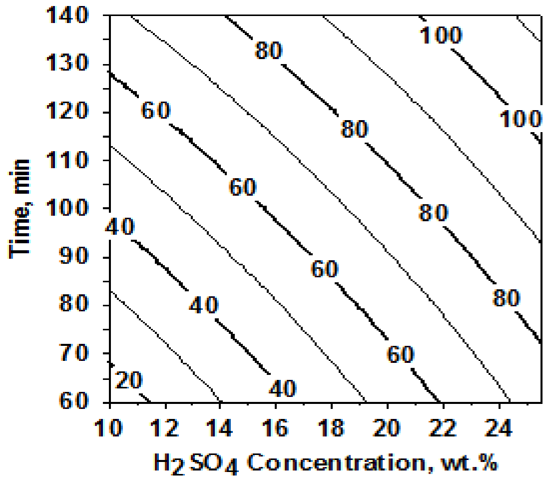

Fig. 7: The Effect of Time and H_2SO_4 Conc. on Mn Recovery %

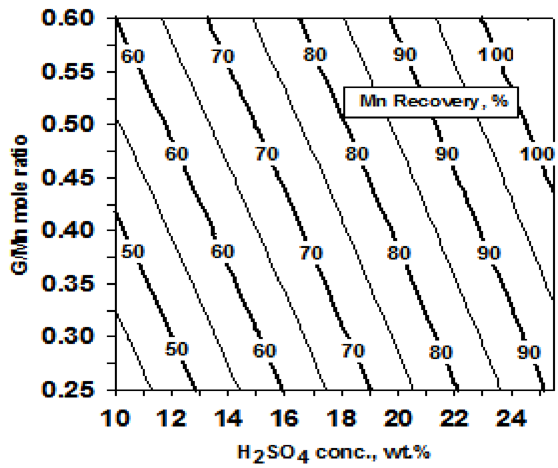

Fig. 8: The Effect of G/Mn Mole Ratio and H_2SO_4 Conc. on Mn Recovery %

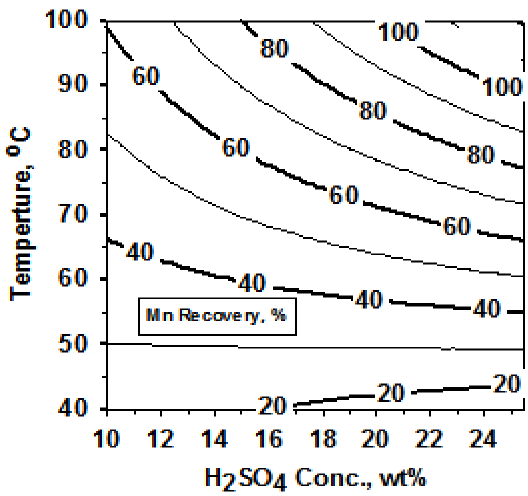

Fig. 9: The Effect of Temperature and H_2SO_4 Conc. on Mn Recovery %

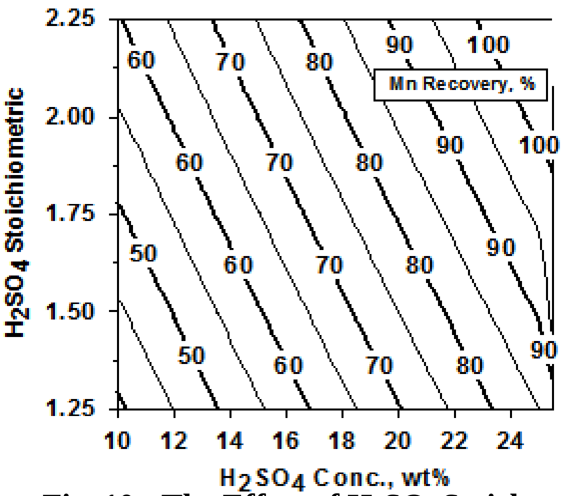

Fig. 10: The Effect of H_2SO_4 Stoich. and H_2SO_4 Conc. on Mn Recovery %