NOVATEUR PUBLICATIONS
INTERNATIONAL JOURNAL OF INNOVATIONS IN ENGINEERING RESEARCH AND TECHNOLOGY [IJIERT]
ISSN: 2394-3696
VOLUME 5, ISSUE 11, Nov.-2018

EXTRACTION OF MAGNESIUM FROM CHROME SLAG BY SULPHIRIC ACID LEACHING AT LOW TEMPERATURES

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ABSTRACT

In this this article ,a solvent extraction method by using sulphuric acid leaching was developed .The process conditions and parameters of sulphuric acid concentration ,leaching temperature ,leaching time and solid to liquid ratio were studied. These studied conditions and parameters were varied from 0.5M to 5M at 0.5 M interval, 30°C to 60°C at 5°C interval and 30 minutes to 240 minutes at 30 minute interval respectively. The solid to liquid ratios used were 1:2, 1:3, 1:4, 1:5, 1:6, 1:7, 1:8, 1:9, 1:10.The optimum percentage extraction efficiency of magnesium as found to be 66.87% at optimum operating conditions of 4M sulphuric acid concentration 60°C leaching temperature, 120 minutes leaching time and 1:2 solid to liquid ratio.

INTRODUCTION

The lightweight nature of magnesium has led to its demand in the alloy manufacturing industries for parts in motor vehicles, aeroplanes and industrial equipment's, over the years [1, 2, 3].The magnesium metal in solution can be obtained from primary sources such as sea water [4, 5] and brine [4, 6].It can also be obtained from other primary sources such as magnesite ores, dolomite ores and canarllite ores [4]. In secondary sources it is obtained from recycled high grade magnesium and magnesium alloy scrap [5].There are various technologies used for the extraction of magnesium and these are dependent upon the source. These technologies are electrolytic process [6], Pidgeon process [7] and thermal reduction process [8, 9, 10] .The magnesium from sea water[4, 5] and brine [4, 6] is extracted by means of the electrolytic process[4, 6].In the case extraction of magnesium from magnesite ores and dolomite ores or carnallite ores the Pidgeon process is applied [4] .In the case of secondary sources (such as magnesium containing scrap and high grade recycled magnesium [11] .) and some primary sources (such as dolomite and magnesite ores [4]) of magnesium the pyro metallurgical process of thermal reduction is used for extraction of magnesium [5].In the fore mentioned technologies the electrolytic process requires 10.5 to 13.2 kWh/kg Mg produced [4, 12],the Pidgeon process operates at temperatures ranges of 1000 to 1300 ^{o}C [4] and the thermal reduction process operates at 1160^{o}C to 1700^{o}C [9, 10, 13, 14, 7] .The energy requirements as mentioned above indicate that these technologies are highly energy intensive [15, 16, 17]. The high energy requirements in these processes result in elevated production costs rendering the processes economically unsustainable. Due to high market demands for magnesium there is need to search for more alternative sources and sustainable technologies for its extraction from various economic sources. This has therefore kindled interest towards studies into the recovery of magnesium from primary as well as alternative secondary sources [18].

In the pyro metallurgical processing of ferrochrome, slag is obtained as a solid waste which has historically been dumped, piling up in large quantities without any pollution prevention, control or remediation posing hazardous potential to the environment and health [18, 19] .This chrome slag, typically contains various metallic species such as SiO_2, Al_2O_3, MgO, CaO, Cr (in form of unreduced CrO or Cr_2O_3 or entrapped ferrochrome metal) and Fe in quantities of 15 –30, 19 –33, 13–25, 1-5, 1–18 and 1–12 percentage by slag weight respectively [20, 21].This slag is currently produced at a rate of 1.1 to 1.9 tonnes per tonne of ferrochrome produced [22] ,which results to a total of 12 to 16 million tonnes per year of slag produced globally [23].In Zimbabwe ferrochrome is processed at Zimasco ,Kwekwe, pyro metallurgic ally , whereby up to date there are mountainous piles of chrome slag in the vicinity or within the mine complex. Considering the metallic constituents of the slag and the volumes of slag which are dumped implies that there are large volumes of metals which can be recovered and if not they pose an environmental and health threat to the communities in the vicinity or within the mine complex. The large volumes of metallic species stock piled as solid waste can significantly be reduced by processing the slags for metals recovery. This will in turn reduce costs for disposal, lessen the potential for environmental damage, supplement metals production and create new revenue streams for the mine.

In the research work carried out on the recovery of metals from chrome slag, a lot of emphasis has been put on the recovery of chromium at elevated temperatures using solvent extraction techniques [24].Currently to the best knowledge of the researchers and literature survey carried out there is no work being carried out concerning the extraction of magnesium from chrome slag. This magnesium constitutes about 13-25% by weight of the disposed slag [21].The potential of developing other alternative sources of magnesium such as ferrous chrome slag, would provide a significant source of raw material for the local industries. This would cut down on magnesium import costs and has the potential to unlock large tonnages of the value metal.

The aim of this article is to extract magnesium from chrome slag using a solvent extraction technique at low temperatures (i.e with low energy inputs) at a pressure of one atmosphere. The authors investigated the effect of some leaching parameters such as: acid concentration, reaction temperature, reaction time and liquid to solid ratio on the magnesium extraction from chrome slag.

2.0 METHOD

2.1 EQUIPMENT AND MATERIALS

- Wavelength Dispersive X-ray fluorescence (XRF) spectrophotometer, Model: Axios, PANalytical, Netherlands

- Atomic Absorption Spectrophotometer ,Varian Spectrophotometer Model: AA200,Date of manufacture 1997
- Electronic top-loading Sartorius AG Gottingen Electric mass Balance, Model: CP323S, 1997
- Electric muffle heater coupled with stirrer
- What man filter Glass fibre filter paper GF/C diameter 17mm
- Glass fibre What man 3-piece filter funnel
- 75µm Sieves
- 50ml Beakers
- 100ml Graduated measuring cylinders
- Spatulas
- 250 ml Round bottomed flask
- Glass Mercury Thermometer (0°C-110°C)
- +250 ml Buchner flask
-

2.2 REAGENTS

- Sulphuric acid (H_2SO_4), AR 98% supplied by Merck
- Distilled water
- Ferrous chrome slag
-

2.3 FERROUS CHROME SLAG SAMPLING

The ferrous chrome slag samples used in this study were collected directly from Zimasco (Kwekwe, Zimbabwe). 20kgs of ferrous chrome slag were sampled randomly from 4 different tailings dam. A composite sample from the four 20 kg bags was made from which 10 kg of sample was obtained using the cone and quarter method of sampling. The 10 kg of ferrous chrome slag sample was then put into a 10kg plastic bag which was then sealed and devoid of air to avoid external contamination. The sealed plastic bag was stored in a dark, cool cupboard away from any heat source, direct sunlight or fluctuating temperatures.

2.3.1 PREPARATION OF FERROUS CHROME SLAG SAMPLE

The ferrous chrome slag collected in section 2.3 was pulverised and sieved using a 75 microns sieve. The underflow ferrous chrome slag sample was heaped and mixed thoroughly. A cone and quarter method of sampling was applied to collect 5 x 32g samples of a homogenous ferrous chrome slag mixture which were taken for X-Ray fluorescence Analysis.

2.3.2 EXPERIMENTAL PROCEDURE

i. 100ml of 1M sulphuric acid were poured into a 250 ml round bottom flask
ii. The flask from (i) was inserted into an electric muffle heater and heated to a temperature of 30°C
iii. A magnetic stirrer was put into the flask in (ii) and 10g of slag from section 2.3.1 were added into the flask
iv. The mixture in (iii) was agitated at 100 rpm for 30 minutes
v. After 30 minutes the flask was removed from the electric muffle heater and the mixture was filtered using a glass fibre What man 3-piece filter funnel.
vi. The filtrate was poured into a 50ml beaker and left to cool in a desiccator
vii. The filtrate from (vi) was analysed for magnesium using an Atomic Absorption Spectrophotometer.
viii. The experiments were repeated following the same procedure from stage i-vii changing the acid concentration from 1M -5.5M at 0.5M intervals, temperature from 30 - 60°C at 5°C intervals, time from 30minutes - 240 minutes at 30minute interval and mass at 10g to 90 g at 10g intervals.

3.0 RESULTS AND DISCUSSION

3.1 XRF CHROME SLAG ANALYSIS

The Chrome slag XRF analysis results obtained on the chemical analysis of the samples carried out in Section 2.3.1 are shown in **Table 1.**

Table 1: Chrome Slag XRF Analysis results

Compound	**Average composition (% wt.)**
SiO_2	31.3977
MgO	26.3939
Al_2O_3	18.0176
Cr_2O_3	14.3476
Fe_2O_3	4.4239
CaO	3.2522
TiO_2	0.5560
Other	1.6111

The results in Table 1 show the average composition of the various constituents of chrome slag from Zimasco Kwekwe determined using the XRF Spectroscopy Analysis.
The results in table 1 indicate that the compounds in abundance are SiO_2 and MgO in quantities of 31.3977 wt. % and 26.3939 wt. % respectively. The quantity of MgO determined in this study is slightly higher than the range of 13-25% for primary sources determined by other researches. [20, 25, 22].The quantity of magnesium (26.3939wt %) in the characterised chrome slag is large compared to the one found in primary sources which are dolomite (13.8wt %) and seawater (0.13%) [21].Therefore chrome slag can be a vital secondary source for magnesium. The other metals of importance available in high quantities are Al_2O_3 and Cr_2O_3 in the quantities of 18.0176% and 14.3476 % respectively

3.2 DETERMINATION OF OPTIMUM LEACHING CONDITIONS

3.2.1 EFFECT OF LEACHING TIME

The results obtained from the experiments carried out in **section 2.3.2** for optimising time are well illustrated in the **fig. 1.** below.

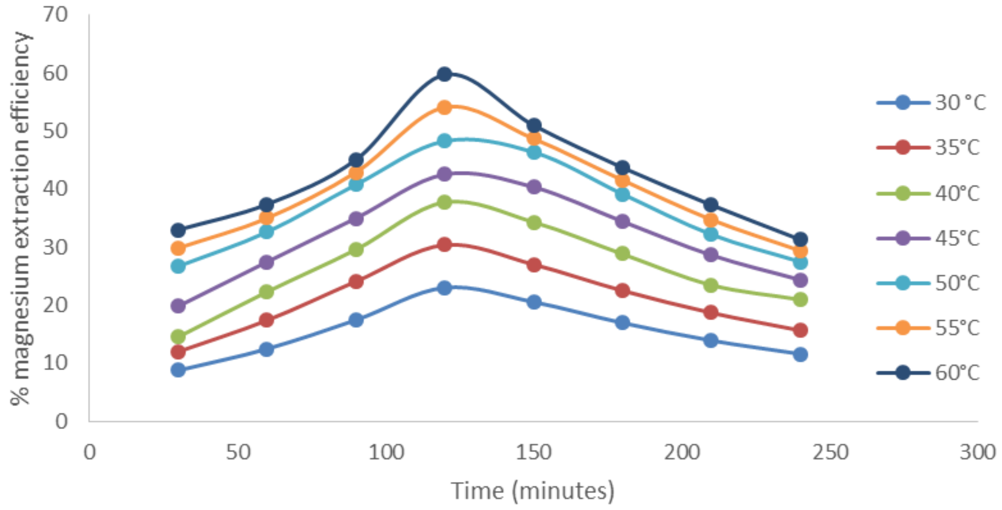

Fig. 1. The graph of percentage magnesium extraction efficiency against leaching time for varying temperatures.

The graphs shown in fig. 1. illustrate the trend of percentage magnesium extraction efficiency with leaching time for varying leaching temperatures for constant acid concentration of 3M, constant solid/liquid ratio of 1:4 and a constant pressure of 1 atm .The graph depicts that the percentage magnesium extraction efficiency increases up to a maximum which is denoted by the peak and gradually decreases as the leaching time increases. The peak/maxima is at a leaching time of 120 minutes. The peaks of the graphs of varying temperatures all coincide at a leaching time of 120minutes, and these peaks denote the maximum percentage magnesium extraction efficiency for each temperature. Therefore the optimum leaching time is 120 minutes. At a leaching time of 120 minutes the highest magnesium extraction efficiency is 55.718% at a temperature of 60°C.If the extraction is carried out in two stages in series at a leaching time of 120minutes, acid concentration constant at 3M, solid to liquor ratio at 1:4 and temperature at 60 °C at a constant pressure of 1atm then 100% extraction of magnesium will be achieved. Therefore the leaching temperature of 60°C can be considered as the optimum low temperature for attaining 100% magnesium extraction in a two stage in series extraction process.

3.2.2 DETERMINATION OF ACID CONCENTRATION AND SOLID LIQUID RATIO

The optimum acid concentration and optimum solid to liquid ratio was obtained by plotting results obtained from section 2.3.2 of percentage magnesium extraction efficiency for varying acid concentrations for different solid to liquid ratio at a constant optimum temperature of 60°C, optimum leaching time of 120 minutes ,at a constant pressure of 1 atm and varying solid to liquid ratio. The graphs are illustrated in fig. 2.

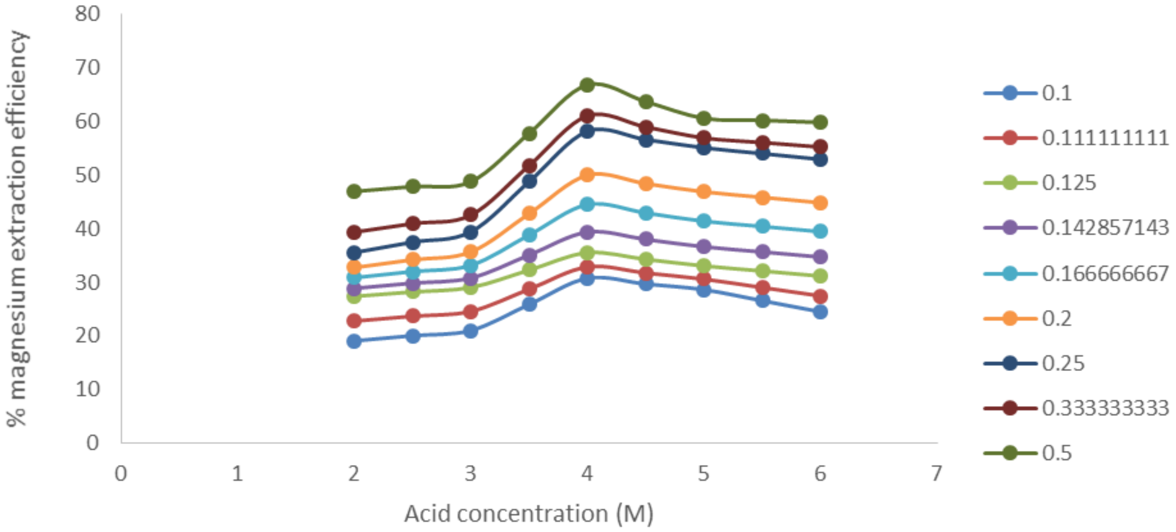

Fig.2. Graph of percentage magnesium extraction efficiency against sulphiric acid concentration for varying solid/liquid ratios.

The graphs in figure 2 illustrates the tendency of percentage extraction efficiency with increase in acid concentration for different solid to liquid ratios at a constant leaching time of 120minutes ,constant leaching temperature of 60°C and at a constant pressure of 1 atm. The graphs show that the percentage magnesium extraction gradually increases up to a maximum which is marked by a peak and then gradually decreases as the acid concentration increases for varying soli/liquid ratios. All the graphs for the different solid to liquid ratio have the maxima coinciding at an acid concentration of 4M.Therefore the optimum acid concentration for percentage maximum magnesium extraction efficiency for the different solid to liquor ratios at 120 minutes leaching time, 60 °C leaching temperature and at 1atm is 4M.

The maxima which denotes the maximum percentage magnesium extraction for different solid to liquid ratio, indicate that solid to liquid ratio of 1:2 (0.5) has the highest value of percentage magnesium extraction efficiency at 4M as compared to the other solid liquor ratios .Therefore the solid to liquid of 0.5 is the optimum solid to liquid ratio. The optimum percentage magnesium extraction efficiency is 66.87% at an optimum leaching temperature of 60°C, leaching time of 120minutes, sulphuric acid concentration of 4M and at a pressure of 1 atm.

4.0 CONCLUSIONS

In this article it can be concluded that the optimum leaching temperature, time, acid concentration , solid to liquid ratio, percentage magnesium extraction efficiency at a pressure of 1atm are 60°C, 120 minutes, 4M , 0.5 and 66.87% respectively. The 100% magnesium extraction efficiency can be achieved if the extraction is carried out in two stages in series. .

5.0 ACKNOWLEDGEMENTS

The authors would like to thank ZIMASCO, Kwekwe, Zimbabwe for allowing ferrous chrome slag samples to be collected from the factory, Chemical Engineering and the Applied Chemistry Department for providing the necessary resources to carry out the research study.

REFERENCES

[1] M. B. Ebert T, "Properties, applications, potential," University of Clausthal Sachsenwey, Department of Material Science, Zellerfield,Germany, 2001.

[2] J. Wileken, "Magnesium -Vefugbarkeit," Clausthal-Zellerfield, 31/10/1999.

[3] W. Wulandan, "Magnesium; Current and alternative production," in Australasion Conference on Chemical Engineering, University of Wollon.

[4] B. G. M. Wulandari W, Mgnesium; Current and alternative prodction routes, University of Wollongong , 2010.

[5] M. L. Chamini A.S, "Magnesium recycling-To grave and beyond," vol. 65, no. 16, pp. 1283-1284, 2013.

[6] G. J. Kipourous, "Advances in molten salt chemistry," 1987.

[7] L. Pidgeon, "New methods of production of magnesium," The Canadian institute of minning and metallurgy, vol. 47, pp. 16-34, 1994.

[8] F. Habashi, Magnesium Handbook of Extractive Metallurgy, Wiinheim Wiley -VCH, 1997.

[9] W. P. M. Brooks G, "Carbothemic Route to magnesium," Journal of Minerals,metals and dolomite materials society , vol. 5, no. 5, pp. 51-55, 2006.

[10] M. J. Faure C, "Magnesium by Magnetherm process," Journal of metaks, pp. 721-723, 1964.

[11] X. Guan, "An environmentally friendly proess involing refining membrane based electrolysis for magnesum recovery of partially oxidised scrap alloy," Journal on Metallurgy, 2013.

[12] J. W. Evans, "The evolution of technology for light metals over the ast 50 years :Al,Mg,Li," Journal of the minerals ,metals and materials society, vol. 59, no. 2, pp. 30-38, 2007.

[13] A. Scoukens, "Technoloical breakthrough of the Mintek Thermal magnesium process." The Journal of South Africa Institute of minning and mettallurgy, vol. 106, pp. 25-29, 2006.

[14] M. Wadsley, "Magnesium metal by the Heggle-loloire process magnesium technology," The mineral and material society, pp. 65-70, 2000.

[15] G. J. Simandl, "Magnesium:Raw materials,metal extraction and economics Globl picture.," British Colombia Ministry of energy,mines and petroleum resources, Victory B.C Canada, 1996.

[16] R. M. Cherubin F, "LCA of magnesium production technological overview and estimation of environmental burdens," Resources conservationand Recycling, vol. 52, no. 8-9, pp. 1093-1100, 2008.

[17] R. W. Norgate T.E, "Assesing the environmental impact of metal production processs," Journal of cleaner production, vol. 15, no. 8-9, pp. 838-848, 2007.

[18] H.-J. Son, "Leaching characteristics of magnesium from mine residuess by sulphiric acid ad nitric acid," Proceedings of the world congress on new technologies, vol. 4, no. 187, 2015.

[19] P. Chandra, "Recvery of chromium from ferrochrome slag," International Journal of innovative research in Science, Engineering and technology, vol. 4, 2015.

[20] A. Kanorbaeva, "Petrographic analysis of Low Carbon ferrochrome slag," Chemical institute, Karaganda.

[21] M. Nkohla, "Characterisation of ferrochrome smelter slag and its implictions in metal

accounting.Master Thesis," Cape Pensinsula University of Technology,South Africa, 2006.

[22] A. Zhdanov, "Wastes Generation and use in ferroalloy production," Institute of Materials science and metallurgy ,Russia.

[23] P. Richard, "Overview of the global hrome market," in INDINOX Stainlesssteel coference, Ahmedabad, 2015.

[24] C. P. Hariharon, "Extractionof chrome from ferochrome slag," Journal of Chemical Engineering and its Applications, vol. 1, no. 3, pp. 1-6, 2016.

[25] A. B. Nilamadhaba Sahu, "Mineral processing and extractive metallurgy eview," vol. 37, India, 2016, pp. 211-21.