

SUSTAINABLE USE OF NATURAL SOURCES & RECYCLING

H.L. Hoşgün¹, H. Kurama²

¹Eskişehir Osmangazi University Chemical Engineering Department, Eskişehir Turkey.

²Eskişehir Osmangazi University Boron Research Center

Abstract

Treatment of metal contained waste became an important discipline in the field of metallurgy due to the recent stringent environmental legislations, increased metal prices on market and securing and continues access to raw materials. Each year mining and extraction industries produce several billion tones of solid inorganic waste or by products during the mineral processing and metal production operations. As a result, recycling or development of “zero waste” innovative beneficiation methods could be an efficient way to decrease the stockpiles of waste resultant from mineral and metallurgical industries.

In this paper the importance of the recycling for sustainable use of natural resources and environment and used treatment techniques are briefly discussed. The specific attention has also been paid to extraction of Mg by HCl leaching from waste dust generated during sintered of magnesium. The effects of treatment test parameters such as chemical composition extraction time and extraction temperature on extraction recovery were discussed. Two level factorial designs were used to determine effects of the test parameters and their interactions on Mg extraction.

Key words: Sustainable, recycling, leaching, Mg, factorial design

1. INTRODUCTION

The EU Directives 2006/12 and revised version of 2008/98 on waste management has generated practical actions on the matter of waste regulations in landfill disposal. These regulation strongly advice the prevention of landfill disposal should be the first priority of waste management, and that re-use and material recycling should also be preferred to energy recovery from waste, where and insofar as they are the best ecological option in order to conserve natural resources [1].

The Organization for Economic Cooperation and Development (OECD) recently reported that the amount of waste generated in Europe has reached to 1.3 billion tones and estimated that at 2020 this amount will be 45% more than in 1995. A period of 1990 and 1995 the generated waste was mainly burnt in incinerators, or dumped into landfill sites (67%). However the following monitoring showed that these methods create environmental damage. Land filling not only takes up more and more valuable land space, it also causes air, water and soil pollution, discharging carbon dioxide (CO₂) and methane (CH₄) into the atmosphere and chemicals and pesticides into the earth and groundwater. This, in turn, is harmful to human health, as well as to plants and animals. Within the resultant waste from domestic, agricultural, electrical and electronic equipment, packing or oily waste, the waste from mining and extraction industries could be handled specially due to the both environmental and economic necessities [2]. In order to maintain the sustainable and cost efficient use of natural resources, new technologies included the re-use of wastes, preparing for re-use treatment and recycling for minimization of industrial waste must be developed instead of the land filled. This could be a beneficial way to decrease the increased stockpiles of waste resultant from mining and metallurgical activities.

2. RESOURCE EFFICIENCY & RECYCLING

This issue clearly defined in the 6th Environmental Action Plan (EAP) as a key parameter to ensure the consumption of resources and their associated impacts do not exceed the carrying capacity of the environment and breaking the linkages between economic growth and resource use. It was stated that the general aim of the Strategy on Sustainable Use of Natural Resources is "to develop a framework and measures that allow resources to be used in a sustainable way without further harming the environment", while achieving the objectives of the Lisbon strategy (3% economic growth) [3,4].

A recent report released by European Technology Platform on Sustainable Mineral Resources (ETP SMR), Strategic Research Agenda-March 2009, was also support the above statement and advised that the "Thematic Strategy" on the sustainable use of natural resources should be based on three pillars to manage the implementing of the strategy in securing access to raw materials which are essential for further development of EU economy. These pillars defined as;

- Fair access to raw materials on world markets,
- The right framework to foster sustainable supply of raw materials from EU sources,
- Increased resource efficiency and promoting recycling in the EU.

The third pillar of the EC Communicate on RMI underlines the need to support recycling, substitution and the increased use of renewable raw materials. That should be promoted in view of easing the critical dependence of the EU on primary materials, reduce import dependency, and improve the environmental balance, as well as meeting industrial needs for raw materials. Strategies to enhance recycling and reuse are important to address social and economic development in a context of restricted access to resources and high import dependency. The advantage of recycling is that it contributes to energy efficiency, particularly in the case of metals where production on the basis of secondary raw materials (scrap) is significantly more energy efficient compared to primary raw material [5].

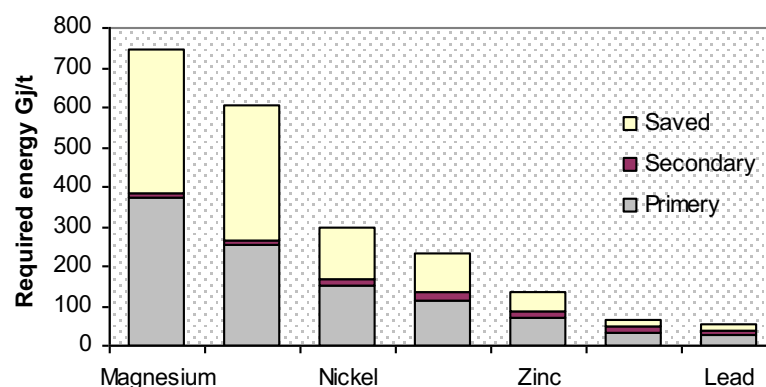


Fig. 1. Energy savings of metal productions from secondary materials

Figure 1 indicates that the accessible energy savings for magnesium and aluminum are remarkably higher compared other metals if secondary sources (slug, waste dust i.e.) are concerned for production.

This can be attributed the high energy requirements of conventional metal production methods both beneficiation and extraction of raw materials [6].

The common goal concerning reuse and recycling within the ETP SMR is to make certain that Europe in 2030 has a recycling industry as a natural part of its mining, mineral and metallurgical industry

In general route for the recycling of valuable minerals /metals from waste, a scrap metal in a solid form is subjected to pyrometallurgical recycling route while if that arising in liquid form such as spent electrolytes from electrochemical processing of metals is recycled by hydrometallurgical methods. The main methods for the extraction of the dissolved metal from process effluents are; precipitation of target metal or metals from sludge by addition of precipitation reactive or extraction of selected metal by using ion exchange, solvent extraction, adsorption, membrane filtration and flotation. In literature several research studies and patents are addressed to application of these techniques for the separation or recovery of the secondary metal from waste material. Recently a review of the benefit of using secondary metals on environment and most practiced recovery processes are presented by Wernick and Themelis [7]. Although the first priority for the extraction or recovery of metals from solid waste is pyrometallurgy, in last years, the field of applicability of hydrometallurgy has been considerably extended its application areas including both solid and liquid waste recycling due to the many potential benefits such as a low investment cost and avoidance of gaseous emissions in the environment, applicability to an increasingly varied range of waste material recovery/recycle in fine size range and selectivity. Hydrometallurgy has accepted most important method in extractive metallurgy since the 1980s. Hydrometallurgy is not only a purification or metal winning step in the value chain, but it is also used for the direct recovery of metals from ores or concentration at mine sites, thus replacing traditional concentrator-smelter routes. The smelters of large units are able to treat different concentrates / or waste and in high quantities and the produce the main metal with a wide portfolio of by products, thus giving a robust and competitive route in the metals production value chain. However, pyrometallurgy cannot refine the metal alone due to low selectivity and therefore hydrometallurgical purification or electrolytic refining is also needed to produce commercial grade metal [8].

3. A CASE STUDY

Magnesite mineral is the basic raw material for the manufacture of alkaline refractories and used in the iron-steel, cement, glass, sugar, ceramic and paper industry. In addition it is also find an application in the paint and ink industry, pharmaceutical as an anti-acid and in the production of many magnesium chemicals and alloys [9]. Turkey has about 160 million tons of world reserve (Table1). Like other countries such as Brazil, Australia, Russia and Slovakia the magnesite producers in Turkey planned to starts production of fused magnesia and increase production capacity for dead-burned magnesia and magnesia-base refractories by year end. MAŞ magnesite company one of the bigger sintered magnesia producers of Turkey [10]. The company processes yearly 150000 tones of sintered product. The traditional method to produce sintered or calcined magnesite includes crushing, screening, drying, classification, magnetic separation and sintering/calcining at horizontal rotary furnace. During this route, every year, the amount of waste material collected in the furnace electrofilters, apprx. 20 000 tones, obtained from sintering plant has being progressively increased due the lower recycling rate. Rather than above mentioned calcination route, Megnezium metal or MgO can also be produced from raw or waste material by hydrometallurgical way. In which raw materials are leached with suitable reagents, generally HCl than precipitated with bases or as a recently practiced in Slovak Republic, MgCl solution refined by precipitation, filtration, and extraction and received MgCl is pyrohydrolysed to produce MgO [11].

Table 1. World Mine Production, Reserves, and Reserve Base at 2008 [10]

Country	Reserve base 1000 t	Production 1000 t
United States	15.000	340
Australia	120.000	140
Austria	20.000	200
Brazil	65.000	100
Chine	860.000	2000
Greece	30.000	150
India	55.000	105
Korea-North	750.000	350
Russia	730.000	350
Slovakia	320.000	170
Spain	30.000	150
Turkey	160.000	600
Others	440.00	140
Total	3600.000	4795

3.1. Materials & methods

The waste samples used in the laboratory dissolution experiments was taken from the different part of the electrostatic bag house of MAS Company, Eskişehir-Turkey. The chemical composition (determined by XRF) of representative samples, desinated as EFDS-1 (AED), EFDS-2(ASD), is given in Table 2. The identification of crystalline material phases in samples, performed with an S5000 diffractometer, with a nickel filtered Cu K α radiation, showed that flue dust mainly consists of original raw (MgCO₃) and sintered magnesite; periclase (MgO), and small amount of serpentine (Lizardite) phases.

Table 2. Chemical analysis results of magnesite dust

Oxide composition	EFDS-1 Weight %	EFDS-1 Weight %
SiO ₂	1.45	3.12
Fe ₂ O ₃	0.31	0.46
Al ₂ O ₃	0.07	0.01
CaO	1.79	1.90
MgO	54.8	56.6
LOI	41.45	38.71

The dissolution tests were performed in a 500 ml three necked round-bottom glass reactor placed on a temperature controlled magnetic stirrer. HCl, was selected as leaching reagent and each tests, 5 g sample of sample was added in to the 250 mL acid solution. Thereafter the setting of leach temperature at desired level of 290– 318 K, the solution was continuously stirred at a fixed stirring speed 350 rpm for 1M HCL concentration. Approximately 5 mL of solution was taken at predetermined time intervals and analyzed by complexometric method to find out effect of dissolution paremetres on the recovery of magnesium from waste material.

In order to evaluate factors that influence the percent extraction of Mg, a two level three factors fractional factorial experiment was designed. The factors, temperature, sample type and extraction time which chosen to find out the response as percentage recovery was given at Table 3. Each factor was studied at two levels – low level and high level. The experimental factors (uncoded units) were transformed into coded units and the levels were coded as –1 (low) and +1 (high). The response was expressed as the percent extraction of Mg. MINITAB™ release 15 statistical software was used to create and analyze the experimental data.

Table 3. High and low levels of factors

Factor	Low level (–1)	High level (+1)
Temperature (A) K	290	318
Type (B)	AED	ASD
Time (C) min.	120	240

3.1. Test results

Results for obtained are shown in Table 3.

The extraction efficiency (η) was defined as:

$$\eta = \frac{C - C_F}{C} \times 100 \quad (1)$$

where C and C_F are, respectively, the initial and final concentrations of magnesium species.

Table 4. Design of trial runs (in coded form) for Mg extraction from waste samples in two replicate experiments.

Run	Temperature	Type	time	Yield %
1	-	-	-	60.66
2	+	-	-	85.67
3	-	+	-	67.39
4	+	+	-	86.16
5	-	-	+	76.79
6	+	-	+	86.13
7	-	+	+	78.79
8	+	+	+	86.84

3.2.1. Pareto plot of effect

Pareto plot that visually represents the absolute values of the effects of main factors and the effects of interaction of factors is given at Figure 2.. It can be seen from Fig. 2 that temperature had the greatest effect on the extraction of Mg from waste samples for 95% confidence.

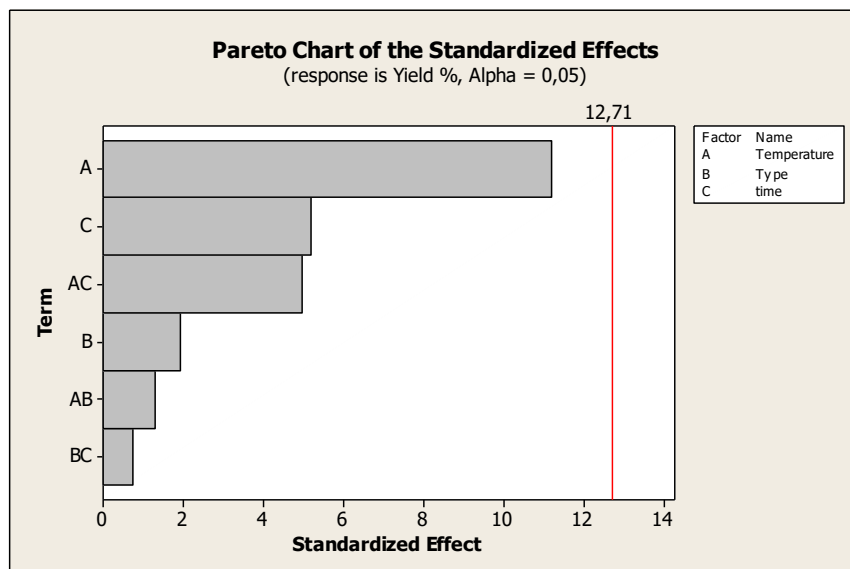


Fig. 2. Pareto chart for standardized effects for Mg extraction.

3.2.2. Main effects plot

The main effects plot represent deviations of the average between high and low levels for each one of them is shown in Fig. 3.

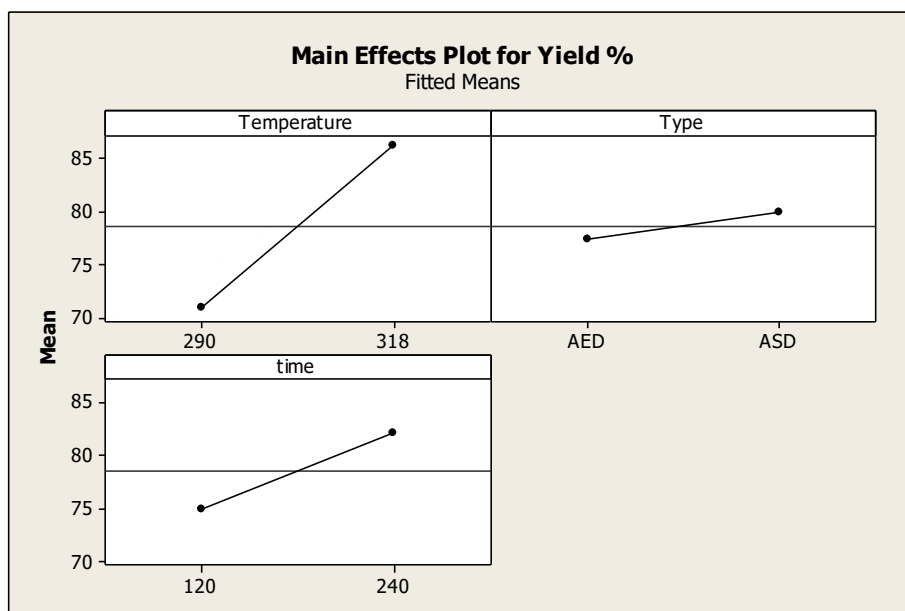


Fig. 3. Main effects plot for percentage Mg Extraction (*Yield %*).

The sign of the main effect indicates the directions of the effect. When the effect of a factor is positive, extraction efficiency increase as the factor is changed from low to high levels. In contrast, if the effects are negative, a reduction in extraction efficiency occurs for high level of the same factor. It can be seen from Fig. 3 that the type of used sample has a smaller change or un- significant effect on the extraction. On the other hand, the effect of temperature was characterized by a greater degree of departure from the overall mean. The extraction percentage of Mg is positively increased by increasing temperature.

3.2.3. Interaction effects plot

The interaction effects plots are shown in Figs. 4 for concerning experimental design. The plots provide the mean response of two factors at all possible combinations of their settings. If the lines are not parallel, it is an indication of interaction between the two factors [12]. The interaction plots showed that rather than temperature, all other factors do not considerable interaction for concerning factors on extraction.

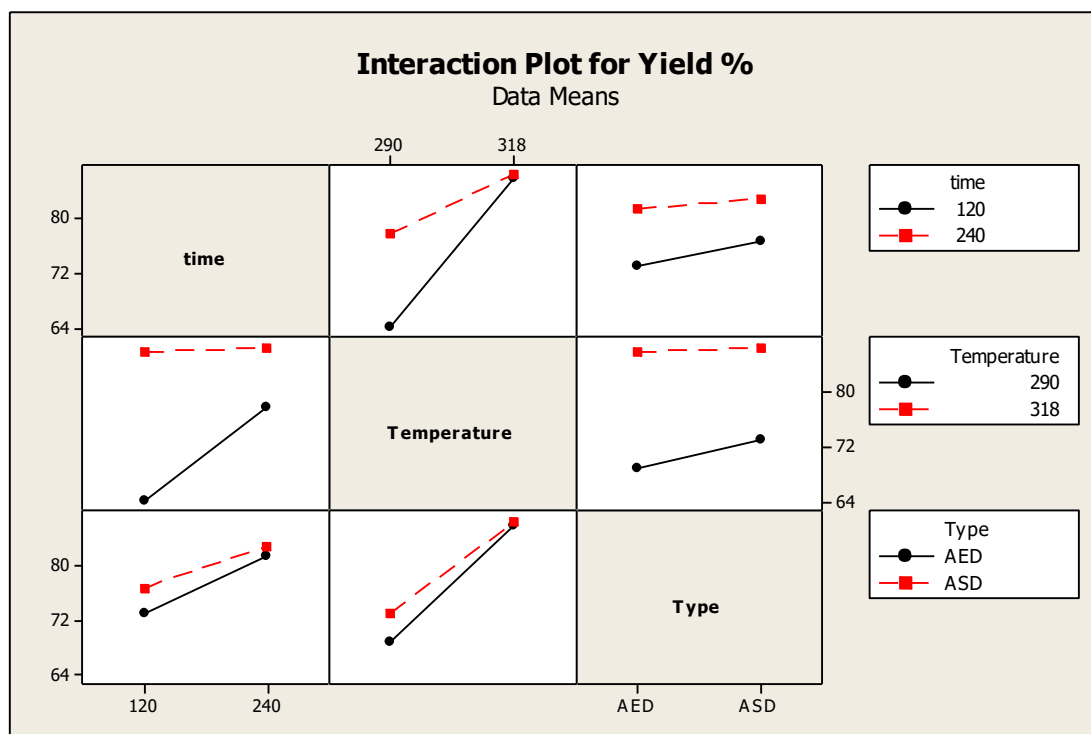


Fig. 4. Interactions effects plot for percentage Mg Extraction (%Yield)

3.2.3. Analysis of variance (ANOVA)

Then after analyzing of the factors main and interaction effects, the determination of the significant factors affecting the extraction efficiency was performed by analysis of variance (ANOVA). In Table 4 the sum of squares used to estimate the factors' effects and the F -ratios (F_0) that defined as the ratio of the respective mean-square-effect and the mean-square-error. Since $F_{0.05,1,7} = 5.59$, all effects presenting F_0 higher than 5.59 have statistical significance. Furthermore, because the factors in this study have two levels, each ANOVA main effect and interactions effects have one degree of freedom. From the P values, defined as the smallest level of significance leading to rejection of the null hypothesis, it appears that the main effect of each factor and the interaction effects are statistically significant when $P < 0.05$. For the concerning experimental design, the variance analyses results showed that any P values lower than the 0.05 however it is nearly approach statistical significance level of 0.05 for the effects temperature.

Table 5. Analysis of variance

Source	Degrees of Freedom	Sum of Squares	Mean Square	F	P
Temperature	1	467.72	467.72	152.71	0.051
Type	1	12.33	12.33	4.02	0.294
Time	1	102.75	102.75	33.55	0.109
Temperature*Type	1	7.09	7.09	2.31	0.370
Type*time	1	2.54	2.54	0.83	0.530
Temperature*time	1	87.05	87.05	28.42	0.118
Error	1	3.06	3.06		
Total	7	682.54			

$$S = 1.75009, R^2 = 99.55\%, R^2_{\text{adj}} = 96.86\%$$

$$\eta = 78.496 + 7.589A + 1.299B + 3.526C - 0.884 AB - 3.356AC - 0.506BC$$

According to the above findings it can be concluded that only the temperature of the dissolution has a main effect on the extraction. The composition of samples was not strongly affected. This result confirms the finding determined at previous study [13] performed to find out the dissolution behavior of electro-filter magnesite dust sample- kinetic analyses.

4. CONCLUSIONS

Each year mining and extraction industries produce several billion tones of solid inorganic waste or by products during the mineral processing and metal production operations. In order to maintain the sustainable and cost efficient use of natural resources, new technologies including the re-use of wastes, preparing for re-use treatment and recycling for minimization of industrial waste must be developed instead of the land filled. This could be a beneficial way to decrease the increased stockpiles of waste resultant from mining and metallurgical activities.

A case study, investigated to test the usability of electro-filter magnesite dust sample, in HCl solution was investigated at the various parameter levels showed that waste magnesite dust can be used instead of raw magnesite deposits to derivation of MgCl as a first step of the production of MgO. From the standpoint of statistical analysis, it is determined that temperature of the dissolution has a positive main effect on dissolution. On the one hand, the interaction between the temperature and contact time of dissolution reactive contributes to extraction of Mg from waste samples.

REFERENCES

1. http://ec.europa.eu/environment/waste/framework_directive.htm

Journal of International Scientific Publication:
Materials, Methods & Technologies, Volume 4, Part 2

2. <http://ec.europa.eu/environment/waste/index.htm>
3. Voet, E van der, Oers, L. van, Sander de Bruyn, Jong, F. de and Tukker A. Environmental Impact of the use of natural resources and products. Report 184
http://www.leidenuniv.nl/cml/ssp/publications/eurostat_indicators_final_report_version_141009.pdf
4. Christmann, P., Arvanitidis, N., Martins, L., Recoché, G. and Solar, S. Towards the Sustainable Use of Mineral Resources: A European Geological Surveys Perspective. Minerals & Energy -Raw Materials Report, 2007; 22: 3, 88 -104
5. European Technology Platform on Sustainable Mineral Resources Strategic Research Agenda Revision 3 Version March 2009.
http://www.etpsmr.org/contents/downloadable-documents/Public%20Download%20Area/SRA_Rev3_Vers_3MOD.pdf
6. Moore, J.J. Chemical Metallurgy. Butterworth Heinemann Ltd. Oxford 1993; 322-3228
7. Wernick, I.K. and Themilis, N. J. Recycling Metals for the Environment. Annu. Rev. Energy Environ 1998; 23: 465–97
8. Kunuutila, K. Role of hydrometallurgy in the winning of non-ferrous metals. Proceedings of European Metallurgical Conference 2009, Innsbruck, Austria Vol. 1 P.XIV
9. Erdoğan N. Kümaş elektro filtre manyezit tozu atıklarından magnezyum bileşikleri üretimi. Ph.D. Thesis. 2002, Osmangazi University, Eskişehir, Turkey
10. <http://minerals.usgs.gov/minerals/pubs/commodity/magnesium/mcs-2009-mgcom.pdf>
11. Raschman, P. and Fedorockova, A. Study of inhibiting effect of acid concentration on the dissolution rate of magnesium oxide during the leaching of dead-burned magnesite. Hydrometallurgy 2004; 71: 403-412
12. Antony J., Design of Experiments for Engineers and Scientists, Butterworth- Heinemann, New York, 2003
13. Hoşgün, H.L. and Kurama, H. The effects of chemical composition on the dissolution behavior of electro filter magnesite dust”. European Metallurgical Conference, EMC 2009, Innsbruck, Avusturya, volume 1, 81-93