

R. MUÑOZ ARROYO*, J. C. ESCOBEDO BOCARDO*, D. A. CORTÉS HERNÁNDEZ*, H. M. HERNÁNDEZ GARCÍA*, J. M. ALMANZA ROBLES*, J. DONIZAK**, Z. KOLENDA**

MAGNESIUM REMOVAL FROM MOLTEN ALUMINUM ALLOYS USING ZEOLITE AND ZEOLITE-SILICA MIXTURES

USUWANIE MAGNEZU Z CIEKŁYCH STOPÓW ALUMINIUM PRZY UŻYCIU ZEOLITU I MIESZANIN ZEOLITOWO-KRZEMIONKOWYCH

A novel process to remove magnesium from molten aluminum alloys is presented. Zeolite and zeolite-silica mixtures were injected into the melt using an inert carrier gas. Pure silica was also injected for comparison purposes. Results indicated that zeolite and zeolite-silica mixtures were more efficient to remove magnesium from the alloy used. The values for the reaction rate constants showed that when the 66 wt% zeolite-containing mixture was used, the magnesium removal rate was 1.77 higher than that observed for pure zeolite and 3.46 higher than that corresponding to pure silica. The water content in the zeolite acts as an additional oxidizing agent, increasing the rate of the magnesium removal. Water oxidizes magnesium and aluminum from the molten alloy faster than SiO_2 . An excessive amount of water produces an unacceptable loss of aluminum alloy. The highest magnesium removal efficiency and the lowest loss of aluminum alloy were obtained by using the mixture containing 66 wt% of zeolite.

Keywords: Metals and alloys; Metallurgy; Minerals; Aluminum; Magnesium; Zeolite

W artykule przedstawiono nowy proces usuwania magnezu z ciekłych stopów aluminium, drogą wstrzykiwania zeolitu lub mieszaniny zeolitowo-krzemionkowej w strumieniu gazów obojętnych. W celach porównawczych w badaniach wykorzystano również czystą krzemionkę. Wyniki przeprowadzonych eksperymentów wskazują, że zeolit i mieszaniny zeolitowo-krzemionkowe efektywniej usuwają magnez z badanych stopów. Wartość szybkości usuwania magnezu dla mieszanin zeolitowo-krzemionkowych była 1.77 razy większa niż dla czystego zeolitu, zaś 3.46 razy większa w stosunku do szybkości obserwowanej dla czystej krzemionki. Cząsteczki wody zawarte w zeolicie działają jako dodatkowy utleniacz zwiększając szybkość usuwania magnezu wskutek utlenienia zarówno magnezu jak i aluminium. Najwyższą wydajność usuwania magnezu przy najmniejszej stracie aluminium obserwowano dla mieszaniny zeolitowo-krzemionkowej o zawartości 66% wagowych zeolitu.

1. Introduction

In secondary metal recycling, removal of magnesium is required for producing standardized materials for several casting alloys. The removal of magnesium from aluminum alloy melts is usually performed by chlorine injection. Although the kinetics of the magnesium removal as MgCl_2 is rapid [1], the un-reacted chlorine and the co-product gaseous AlCl_3 limits the environmental acceptability of the process [2]. On the other hand, the electrochemical method constitutes an alternative to remove magnesium from aluminum alloy melts as a pure metal without the generation of hazardous effluents to the environment, however, the high costs for the electricity production makes this method not suitable [3]. Other alternative to remove magnesium from aluminum

alloy melts is the use of solid reactive agents, such as aluminum fluoride and potassium aluminum fluoride. These reactive agents partially decompose into the melt removing magnesium but producing gaseous pollutant emissions [4]. The kinetics of the solid-liquid reactions is relatively slow and it is necessary the use of techniques to achieve increased solid/melt mixing efficiency. Another study, in which SiO_2 is used as solid reactive agent, demonstrated that it is possible to remove magnesium from aluminum alloy melts producing MgAl_2O_4 (solid) and Si (liquid) non-pollutant co-products [5]. In a recent research, submerged SiO_2 injection in an aluminum alloy melt using argon inert carrier gas showed that it is possible to remove magnesium from 1.2 to 0.02 wt% [6]. However, the kinetics of the process was still slow.

* CINVESTAV – UNIDAD SALTILLO, CARR. SALTILLO-MONTERREY KM 13.5, A. P. 663, 25000 SALTILLO, COAH. MÉXICO

** DEPARTMENT OF PROCESS ENGINEERING, AGH – UNIVERSITY OF SCIENCE AND TECHNOLOGY, 30-059 KRAKÓW, 30 MICKIEWICZA AV., POLAND

In order to search for a method that combines higher productivity with environmental acceptability, in this work the use of the submerged solid injection method, using mineral zeolite and zeolite/silica mixtures as a solid reactive agents and argon as a carrier inert gas, is explored. The characteristics of zeolite, such as high specific surface area, ion exchange and reversible dehydration capacities [7] makes this ceramic a promising candidate for magnesium removal from aluminum alloy melts.

2. Experimental Procedure

2.1. Materials

The mineral zeolite and silica were separately crushed in a ball mill and classified obtaining, in both cases, a particle size minor than 150 μ m. A portion of mineral zeolite was dried at 140°C for 16 h and stored in a desiccator. Mineral samples were analyzed by X-ray diffraction and scanning electronic microscopy. The chemical composition of the minerals was determined by atomic absorption spectroscopy, inductively coupled plasma spectrometry and gravimetric method.

The selected alloy was the A332 aluminum base alloy (Al-11.64Si-0.338Fe-2.05Cu-1.00Mg-1.54Ni). Ultra high purity argon was used as a carrier gas.

2.2. Experimental setup

An induction electric furnace, equipped with a silicon carbide crucible of 12 kg of capacity and temperature control, was used to melt the alloy. An injection equipment with devices to measure and control the gas and solid flows was used. The injection lance was made of graphite and covered externally with refractory material. The internal diameter of the lance was 6.98 mm.

3. Submerged solid injection experiments

The selected parameters used for the submerged solid injection experiments were: argon flow of 4.4 l/min,

solid flow of 16.2 g/min, mass of aluminum alloy of 8 kg and aluminum alloy melt temperature of 750°C. The lance was submerged at the 85% of the depth of the melt. The variable in the experiments was the composition of the solid to be injected. Pure mineral zeolite, pure dried mineral zeolite, pure mineral silica, and mixtures of mineral zeolite and mineral silica formulated with 30, 50 and 66 wt% of mineral zeolite were tested. The mass of the solid to be injected was calculated considering that the reactive solid was silica and the reaction products spinel (MgAl₂O₄) and silicon.

For each experiment, samples of the melt were obtained every 10 min and the produced slag was collected at the end of the experiment. The solidified samples were analyzed by spark atomic emission spectrometry to determine their chemical composition and a sample of the slag was analyzed by X-ray diffraction.

4. Results and discussion

The chemical analysis of zeolite and silica used in this work is presented in Table 1.

The results of the XRD analysis, presented in figure 1, indicate that mineral zeolite is composed by (Ca, Na)₂·3Al₃(Al, Si)₂Si₁₃O₃₆·12H₂O (heulandite) and KAlSi₃O₈ (sanidine), and mineral silica is SiO₂ (quartz).

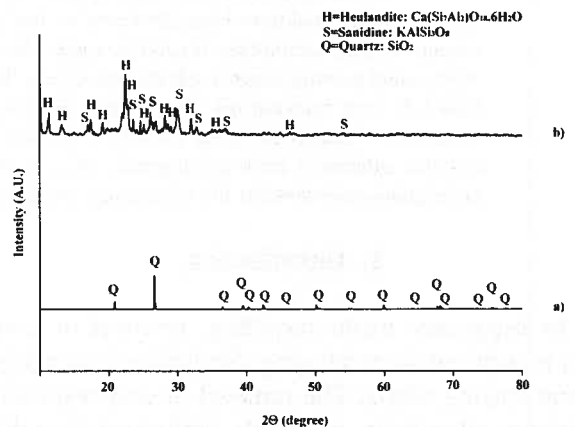


Fig. 1. XRD patterns of (a) mineral silica and (b) mineral zeolite

Chemical analysis of zeolite and silica (wt%)

	K	Ca	Na	Sr	Ba	Al	SiO ₂	Fe	Mg	Mn	CO ₃
Zeolite	1.41	1.43	0.058	<0.005	<0.005	6.08	56.09	1.51	0.40	—	<0.001
Silica	0.004	0.059	0.022	<0.20	<0.20	0.155	99.19	0.080	0.010	—	0.070

Figure 2 shows the magnesium content in the aluminum alloy melt as a function of the injection time for the different solid compositions tested during the injection

experiments. It is possible to observe that the lowest magnesium removal yields were obtained in the experiments in which dried zeolite and silica were used. The

TABLE 1

highest magnesium removal yield was obtained by using the 66 wt% zeolite-containing mixture. As the zeolite content in the mixture increases the magnesium removal yield is increased until a maximum is reached. If the zeolite content in the mixture exceeds 66 wt%, the magnesium removal yield decreases. Assuming a first order irreversible reaction [6], the values for the reaction rate constants for each experiment were calculated and are presented in Fig. 2. According to these values, when the

66 wt% zeolite-containing mixture is used, the magnesium removal rate is 1.77 higher than that observed when pure zeolite is used and 3.46 higher than that corresponding to pure silica. Another parameter, measured at the end of each experiment, was the loss of aluminum alloy by oxidation. The losses were of 22.5, 16.5 and 12.3 wt% when silica, zeolite and the 66 wt% zeolite-containing mixture, respectively, were used.

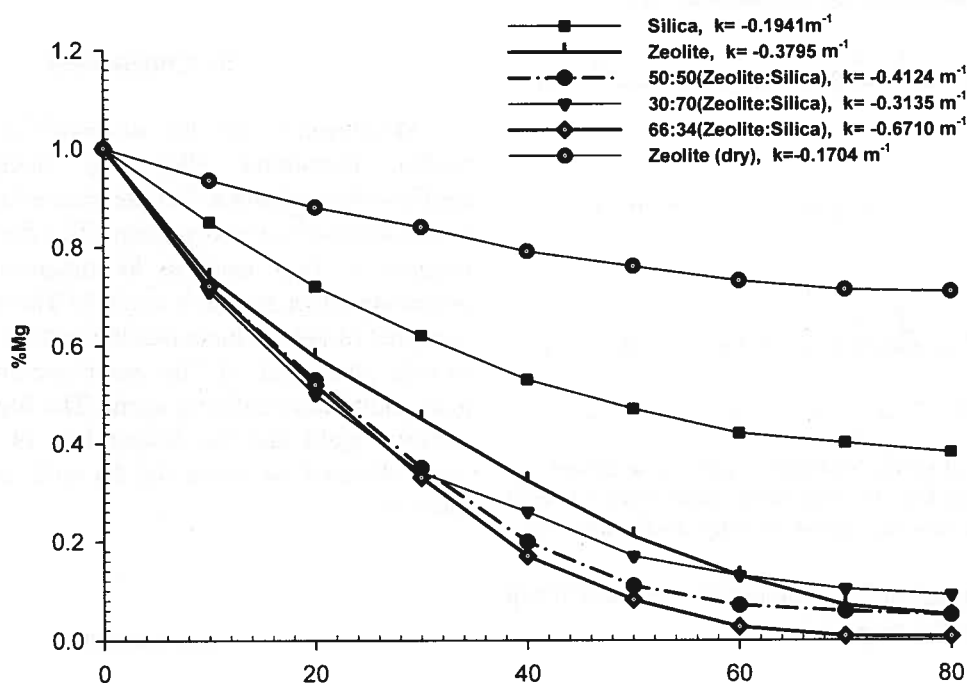


Fig. 2. Injection experiments: magnesium content vs. injection time for the different solids tested

Figure 3 shows the SEM image of a semi-reacted silica particle. It is possible to observe two zones, a nucleus (B) and a layer of reaction products (A). The EDS spectrum corresponding to zone B indicates that the material is composed of Si and O in a proportion similar to that of silica, indicating that this is an un-reacted silica nucleus. The EDS spectrum corresponding to zone A indicates that the layer contains Al, Mg and O in a proportion similar to that of spinel ($MgAl_2O_4$), which is the final product of the magnesium removal reaction.

Figure 4 shows the SEM image of a semi-reacted zeolite particle. In this case it is also possible to observe a nucleus (B) and a layer of reaction products (A). The elements detected in the EDS spectra of zones B and A suggest that this is an un-reacted zeolite nucleus covered by a spinel layer ($MgAl_2O_4$).

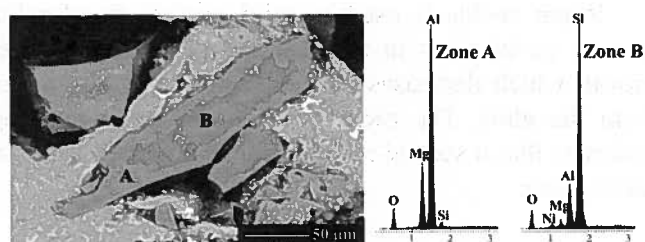


Fig. 3. SEM image and corresponding EDS spectra of a semi-reacted silica particle

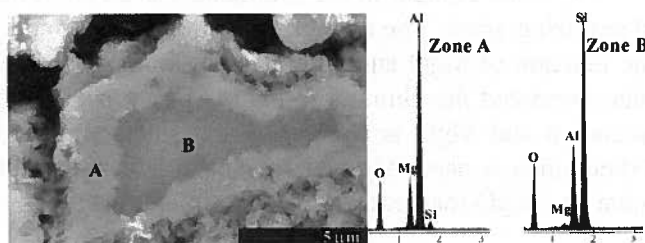


Fig. 4. SEM image and corresponding EDS spectra of a semi-reacted zeolite particle

The XRD analysis of the slag obtained from the

experiment where silica was used (Fig. 5b) indicates the presence of Al, Si, silica and spinel. When zeolite was used, the corresponding slag analysis (Fig. 5c) indicates the presence of Al, Si and spinel. When the 66wt% zeolite-silica mixture was used, the slag analysis (figure 5a) indicates the presence of Al, Si, silica, spinel, periclase and clinoptilolite.

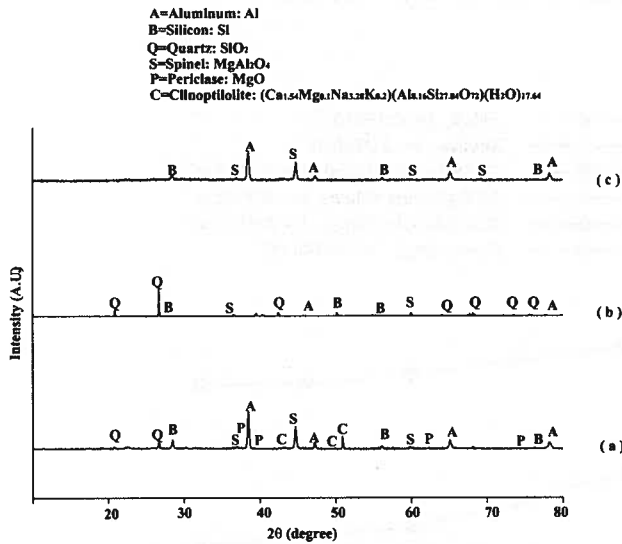
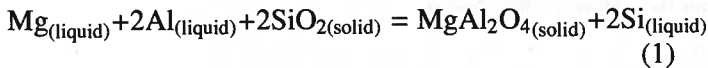
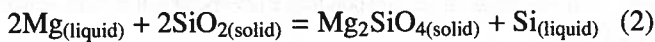


Fig. 5. XRD patterns of (a) slag of 66wt% zeolite-silica mixture was used, (b) slag obtained from the experiment where silica was used and (c) slag obtained from the experiment where zeolite was used

The global reaction for magnesium removal when silica is used as solid reagent is:



When zeolite is used as solid reagent, its alumina content participates in the reaction of magnesium removal, which decreases the consumption of aluminum from the alloy. The presence of forsterite in the slag indicates that a second reaction for magnesium removal takes place:



The water content in the zeolite acts as an additional oxidizing agent. The magnesium removal occurred by the reaction of MgO and alumina. The water in the zeolite promoted the alumina formation by the aluminum oxidation and MgO is formed by the silica reduction. When silica is used, Mg and Al reduce it forming alumina and MgO that react to produce spinel, the reaction

proceeds through a dense layer, reducing the magnesium removal rate. On the other hand, when zeolite is used, the alumina is already intimately linked to silica. As this silica is reduced, the MgO reacts with the alumina present in the zeolite to form a porous reaction layer. Water in the zeolite oxidizes the aluminum, thus as zeolite is reduced in the zeolite silica mixture the aluminum loss is also reduced due to the lower water content. The silica also contributes to the formation of MgO, increasing slightly the magnesium removal rate.

5. Conclusions

Magnesium can be successfully removed from molten aluminum alloys by using zeolite and zeolite-silica mixtures. Zeolite showed to be a more efficient magnesium remover than silica due to the following reasons: a) Two reactions for magnesium removal are occurring when zeolite is used, b) The high specific surface area of zeolite increases the surface for the reactions to take place and, c) The water content in zeolite acts as an additional oxidizing agent. The highest magnesium removal yield and the lowest loss of aluminum alloy were obtained by using the 66 wt% zeolite-containing mixture.

REFERENCES

- [1] Q. Fu, J. W. Evans, Kinetics of magnesium removal from aluminum alloys by chlorine fluxing. In: Light Metals, TMS, 865- 870 (1998).
- [2] D. V. Neff, B. P. Cochran, Chlorination technology in aluminum recycling. In: Light Metals, TMS, 1053-1060 (1993).
- [3] B. L. Tiwari, B. J. Howie, R. M. Johnson, Electrolytic demagging of secondary aluminum in a prototype. In: Transactions AFS, 385-390 (1986).
- [4] T. Lehner, P. J. Koros, V. Ramachandran, International symposium on injection in process Metallurgy. In: TMS, USA;1991 Chapters 1-13.
- [5] Ch. Martinez - Galindo, A Study of the SiO₂ Injection for Magnesium Removal from Liquid Aluminum. In: MSc. Thesis, CINVESTAV Unidad Saltillo, México, 1998.
- [6] J. C. Escobedo, J. F. Hernández, S. Escobedo, A. Flores, D. A. Cortés, Rev. Metal. **39**, 172-82 Madrid 2003.
- [7] Ch. Baerlocher, W. M. Meier, D. H. Olson, Atlas of zeolite framework types: Elsevier, 2001.