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Atmospheric Thermal Magnesium Extraction

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ABSTRACT

A small-scale testwork program was carried out in order to investigate certain aspects of thermal extraction of magnesium at atmospheric pressure. Two series of tests were performed in a 100kVA DC open-arc furnace using dolime or magnesia as the sources of magnesium. In the first series of tests, magnesia-based recipes were charged into the furnace at a rate of about 3.5 to 4.0kg/h and at temperatures of 1705 to 1872 ^{0}C. Depending on the feed mix, nearly 30 to 40 per cent of the contained magnesium reported to the gas phase, leaving a slag analyzing about 55 to 61 per cent MgO.
In the second series of tests, dolime-based feed recipes were reacted at temperatures between 1690 and 1720 ^{0}C and at a feed rate of about 5.8kg/h. Depending on the feed recipe, the calculated magnesium extraction ranged from about 80 to 91 per cent, producing a slag containing 5 to 10 per cent MgO.

INTRODUCTION

Thermal production of magnesium, at normal atmospheric pressure, was demonstrated in the late 1980s by Schoukens (1989). The testwork was carried out in a DC arc furnace at a scale of 50 to 100kVA. The work eventually lead to the inception and patenting of the Mintek Thermal Magnesium Process (MTMP), Barcza, et al (1987), Barcza et al (2000), Barcza, et al (2001).

However, the tests involved injecting argon into the sealed furnace as a means of limiting the magnesium vapour pressure to about 0.3 to 0.5 atm. In several tests, lime or alumina were added as fluxing agents as practiced in the Pechiney process, Artru, et al, (1961).
In order to further advance the MTMP process, it is important to seek alternative feed recipes and process conditions. This is important in order to minimize the operating

cost of production that will allow the MTMP to compete effectively with the ever-expanding Pidgeon process in China, Ding, et al (2001).

Mintek, along with its consortium partners Anglo American and Eskom as well as New World Alloys, therefore have undertaken an R&D program to further advance the MTMP process, where various feed mixtures and operating conditions were examined. The work involved thermodynamic simulations, techno-economic studies and finally, the experimental work. This paper presents the results of the testwork conducted in a 100kVA DC arc facility using various recipes.

EXPERIMENTAL EQUIPMENT

The testwork was carried out in a 100 kVA DC arc facility (Figure 1). The facility consisted of a DC power supply, rated at 1000A and 100V, a refractory lined furnace, a feed system and a gas extraction system.

The furnace shell was made of mild steel shell that was lined with an outer layer of alumina castable and an inner layer of graphite crucible, giving a working furnace diameter of 250mm, with a height of 400mm. The furnace base contained a graphite block (50mm thick and 300mm in diameter). The graphite block was connected to a mild steel bar that acted as the anode. The furnace shell was cooled via a water-cooling jacket.

The roof was lined with high alumina refractory and contained three entry ports, one for gas extraction, a feed entry and a cathode port. A graphite rod (50mm in diameter) was employed as the cathode. The gas extraction system consisted of an off-gas duct, (mild steel, 50mm in diameter), two portable filters each enclosed in a steel housing, and finally a bag house. The feed system was not utilized during the testwork due to the relatively large size of dolime and magnesia and thus the feed recipes were charged into the furnace manually.

EXPERIMENTAL PROCEDURES

The smelting testwork was carried out as follows: a fixed amount of metal heel (see Table 1) was charged into the furnace and an arc was established at a power level of 15 to 20kW. Once a stable arc was maintained, the power was gradually increased to

about 25kW and kept at this level until the metal heel was molten and the bath temperature reached about 1550°C.

The feed recipe was then manually fed to the furnace over a certain period of time. During the feeding period, the furnace power was increased to between 35 and 37kW while maintaining an operating voltage of 75 to 80V. Once the full batch had been charged into the furnace the power (35kW) was kept on for an additional 5-minute period, before switching off to take a pyrometer temperature reading of the bath. At the end of each test, an attempt was made to tap the furnace, with some success. This limited success was mainly due to rapid solidification of the slag as soon as the power was turned off. The furnace was then allowed to cool down overnight before the products were collected, weighed, sampled and analyzed. The tests were carried out in the absence of any inert gas, thus the magnesium vapour pressure inside the furnace was believed to have been at 0.85atm, the local atmospheric pressure.

FEED RECIPES

Various feed recipes were experimented with as shown in Table 1. These recipes were based on the results of extensive thermodynamic simulations using Pyrosim software, Jones (1987), guided by preliminary techno-economic evaluation.

Each batch of a given test was prepared by accurately and separately weighing the feed components, followed by thorough mixing for at least 45 minutes. The batch was then stored in a separate plastic bag that was kept sealed. The magnesia used in Tests 1 to 8 was prepared at Vereeniging Refractories, (VerRef, a South African refractory producer), using a tunnel kiln operated at 1720°C. The dolime (Tests 10 to 12) was also obtained from VerRef and was calcined in a rotary kiln operated at 1400-1500°C. In Test 9, another source of magnesium was obtained from New World Alloys, formerly Mt Grace Resources, and calcined at 1650°C in an induction furnace.

The particle size of dolime and magnesia was between 3 and 25mm. Ferrosilicon and aluminium were employed as reducing agents and had a particle size range of 6 to 12mm. Detailed chemical analyses of the various raw materials appear in Table 2.

In total, eight different recipes were evaluated experimentally. The first four recipes were based on a magnesite ore containing 44.5% MgO and 5.2% SiO_2 (Mag-1 to 4). These tests were performed in duplicate. The fifth recipe was based on a relatively

high quality magnesite ore that analyzed 43.4% MgO and 1.2% SiO_2 (Mag-5). The last three recipes were based on a dolomite ore (Dol-6, 7, and 8).

EXPERIMENTAL RESULTS AND ANALYSES

Chemical analyses of the produced slag are shown in Tables 3. For Mag-1, the MgO content of the slag averaged about 60.4% as compared to about 57.7% in Mag-2 where lime was added with the aim of producing slag containing 10% CaO (actual achieved was about 5.3% CaO). Note that in these two recipes, aluminium and ferrosilicon additions were adjusted to give 12.5% Al_2O_3 in the slag, as predicted by Pyrosim. It appears that the MgO content of the slag decreased with lime addition. This was mostly due to dilution as will be shown later. Increased aluminium addition to obtain 15% Al_2O_3 in the slag (Pyrosim – Mag-3) did not appear to significantly affect the MgO analysis in the slag where it averaged 56.1%, although the magnesium extraction improved somewhat. Eliminating the aluminium from the feed recipe (Mag-4) and the addition of lime, (10% CaO in slag), resulted in a slag containing 55.3% MgO.

Using the high quality magnesia ore (Mag-5) resulted in a slag containing 55.8% MgO (other test conditions are per Mag-4) which was essentially the same MgO level as in Mag-4). As shown in Table 3, the operating temperatures ranged from 1705 ^{0}C (Mag-3, Test 2) to 1872 ^{0}C (Mag2, Test 2), as compared to a target temperature range of 1750 to 1800 ^{0}C.

X-ray diffraction of slag samples taken from four separate tests (namely Tests 2, 4, 5, and 6) suggested the presence of periclase (MgO) and olivine (Mg_2SiO_4), as Figure 2 indicates. This is consistent with Pyrosim predictions and the work by Cameron (1992), and is similar in nature to the phases usually present when dolime is used as the source of magnesium, where Ca_2SiO_4 is formed instead of Mg_2SiO_4, Morsi et al, (2002). Calcium-magnesium silicates were also evident in tests were lime was used. In addition, certain samples contained magnesium-aluminium silicates. The last two observations are based on SEM-EDS analysis.

The last three recipes focused on employing dolime as the source of magnesium. Both FeSi and Al additions were varied to give the same extraction level as predicted by Pyrosim. Based on the analysis of the slag tapped from the furnace, the MgO content increased from 2.6% (Dol-6) to about 5.1 and 7.7% in Dol-7 and Dol-8

respectively. However, samples taken from the dig-out slag showed essentially the same MgO content of about 10%. Note that Schoukens (1989) reported a MgO analysis of about 4.2 to 7.4% in the slag that contained about 14%Al_2O_3. His tests were carried out under a magnesium partial pressure of 0.3 to 0.5atm (balance being argon). The measured operating temperatures of the dolime tests were between 1695 to 1715 ^{0}C, which is close to the target range of 1700 to 1750 ^{0}C

In the case of the magnesia-based recipe, the magnesium extraction was calculated assuming that: 1) all the iron in the feed materials reported to the residual FeSi phase (100% accountability), and 2) the fume contained 100% MgO. The results of these calculations are summarised in Table 4 for each test. Statistically speaking, Mag-1 and Mag-2 gave similar Mg-extraction levels of 24 to 29%. In other words, the presence of lime (Mag-2) did not improve the extraction, but had a positive influence on the flowability (tappability) of the slag as compared to that of Mag-1.

Increasing the aluminium addition (Mag-3) with the aim of getting 15% Al_2O_3 in the slag (vs 12.5% in Mag-1) improved the level of extraction to between 31.4 and 35.0%. Doing so also resulted in a better flowing slag. Elimination of the aluminium from the recipe and producing a slag with 10%CaO (Mag-4), the magnesium extraction improved from about 24.0-29.4% in Mag-2 to over 36.2% in Mag-4.

Note that in Mag-4, more FeSi was added in order to achieve similar extraction to that predicted by Pyrosim. Mag-4 also produced a slag that appeared to be flowable for tapping. The higher MgO-content in Magnesia-2, and its lower SiO_2 analysis, improved magnesium extraction to about 40% in Mag-5, as compared to the result of Mag-4. Note that the produced slag appeared to be tappable.

The dolime-based tests (Dol-6 to 8) showed a gradual drop in magnesium extraction as the aluminium addition was decreased. It should be noted that FeSi addition was varied with the lowering of Al to give the same extraction-level as predicted by Pyrosim. Schoukens (1989) reported a degree of extraction ranging from 84 to 91%, while the Pechiney process achieved about 90% magnesium extraction, Bowman (1985).

However, dig-out slag samples exhibited statistically similar levels of extraction at 70.2 to 72.5% only. It is believed that these samples were contaminated with high MgO-fume that deposited on the upper portion of the sidewalls. The three-dolime recipes appeared to have produced a good fluid slag that could be tapped at a larger

scale. Note that the calculated extraction figures assume that all the calcium in the feed reported to the slag phase.

It should be noted that, with magnesia, the main chemical reaction can be represented by:

$$4MgO + Si = Mg_2SiO_4 + 2Mg(v)$$

Suggesting that magnesium extraction is theoretically limited to 50 per cent. On the other hand, when dolime is employed as the source of magnesium, the reaction is:

$$2MgO + Si + 2CaO = Ca_2SiO_4 + 2Mg(v)$$

allowing high degree of magnesium extraction to be reached under the right experimental conditions.

The average magnesium reaction rate is presented in Figure 3 for the recipes tested. For Mag-1 to 4, the rate was between 8.3 to 10.3 kg/h/m^2 of the furnace hearth area. It increased to about 11.1 kg/h/m^2 in Mag-5, mostly due to the higher MgO content in the magnesia used. Dolime tests resulted in an extraction rate of 18.3 kg/h/m^2 (Dol-8: no aluminium in feed) to over 21 kg/h/m^2 with about 4.6% Al in the feed (Dol-6).

The above rates were based on the entire feeding period for a given recipe, and as such represent the average rate of Mg-extraction. These rates are similar to those achieved when zinc-containing feedstock was smelted using the same facility. Where a typical reaction rate of 20kg Zn/h/m^2 was reached.

In addition to the feed recipes and feed rates, differences in operating temperatures may have influenced the magnesium extraction and its reaction rate, as well as sampling and analytical errors. Also note that the, due to differences in batch masses, the maximum slag depth (end of feeding period) was about 40 to 45mm with magnesia tests, and 110 to 115mm with the dolime tests.

CONCLUSIONS

Magnesium extraction from magnesia was successfully demonstrated in a 100kVA DC arc furnace at a magnesium vapour pressure of 0.85atm. The degree of extraction ranged from 24 to 40%, depending on the feed recipe and the magnesia source. The predicted degree of extraction was 30 to 40 per cent. The magnesium reaction rate averaged about 8.9 to 11.1kg/h/m^2. With dolime, the level of extraction was between about 80 to 91%, resulting in an extraction rate of about 18 to 21kg/h/m^2.

Further testwork in Mintek's pilot plant (at 700 to 900kW-scale) is recommended to confirm the results and to prove the tappability of the slag. Such testwork would also give a good indication of the quality of the crude magnesium that could be produced.

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Table 1. Feed recipes

Recipe No.	Test No.	Magnesia kg	Dolime kg	Al g	FeSi g	Lime g	Metal heel	
							FeSi, g	Mild Steel, g
Mag-1	1 2	2.9 6.0	- -	199 412	346 715	- -	100 300	377 723
Mag-2	3 4	6.0 6.0	- -	381 381	746 746	777 777	300 300	600 600
Mag-3	5 6	6.0 6.0	- -	540 540	715 715	- -	300 300	600 600
Mag-4	7 8	6.0 6.0	- -	0 0	1560 1560	690 690	300 300	600 600
Mag-5	9	6.5	-	0	1870.5	782.5	300	600
Dol-6	10	-	16	864	2020	-	590	910
Dol-7	11	-	16	288	2960	-	590	910
Dol-8	12	-	16	0	3520	-	590	910

Test 1 to 8: *Magnesia-1*
Test 9: *Magnesia-2*
Feed period: *Test 1= 1hour, Tests 2 to 9 = 2 hours, Tests 10-12 =3 hours and 20 minutes*

Table 2: Chemical analyses of raw materials, mass per cent.

Component	Magnesia-1	Magnesia-2	Dolime	Lime	FeSi	Al
MgO	86.80	93.60	39.10	1.55		
Al_2O_3	0.75	0.05	0.48	0.43		
SiO_2	6.90	2.41	0.98	0.90		
CaO	0.71	0.41	56.20	93.80		
MnO	0.46	0.02	0.02	0.17		
Fe_2O_3	2.08	0.47	0.31	2.08		
LOI	0.10	0.10	0.1	NA		
Fe	-	-	-	-	23.00	0.15
Si	-	-	-	-	75.5	0.06
AL	-	-	-	-	0.55	99.75
Mn	-	-	-	-	0.13	0.002
Total*	97.80	97.06	97.19	98.26	99.18	99.62

**Balance: Cr_2O_3, $Ti0_2$, ZrO_2, P_2O_5, alkalis, halides,, etc.*

Table 3. Chemical analyses of the produced slag, mass per cent, and tapping temperatures

Recipe No.	Test No	MgO	Al_2O_3	SiO_2	CaO	Temp. ^0C
Mag-1	1	60.37	12.33	22.40	1.69	NA
	2	60.50	10.30	22.40	0.76	1838
Mag-2	3	57.15	10.90	19.35	4.61	1798
	4	58.20	8.90	20.80	5.97	1872
Mag-3	5	57.10	15.30	26.20	0.75	1844
	6	55.10	16.75	25.85	0.71	1705
Mag-4	7	54.20	1.92	34.00	10.27	1820
	8	56.30	1.80	36.65	8.88	1742
Mag-5	9	55.80	0.52	30.40	9.24	1750
Dol-6	10	2.60 (10.80)	13.60	17.60	55.50	1710
Dol-7	11	5.10 (10.90)	5.78	25.60	52.60	1695
Dol-8	12	7.72 (9.97)	2.56	30.25	50.90	1715

Values in brackets are based upon dig-out slag analysis

Table 4. Calculated magnesium extraction, per cent

Recipe	Test No	Extraction
Mag-1	1	28.1
	2	29.9
Mag-2	3	24.0
	4	29.4
Mag-3	5	31.4
	6	35.0
Mag-4	7	35.5
	8	36.6
Mag-5	9	40.0
Dol-6	10	91.3
Dol-7	11	86.1
Dol-8	12	79.1

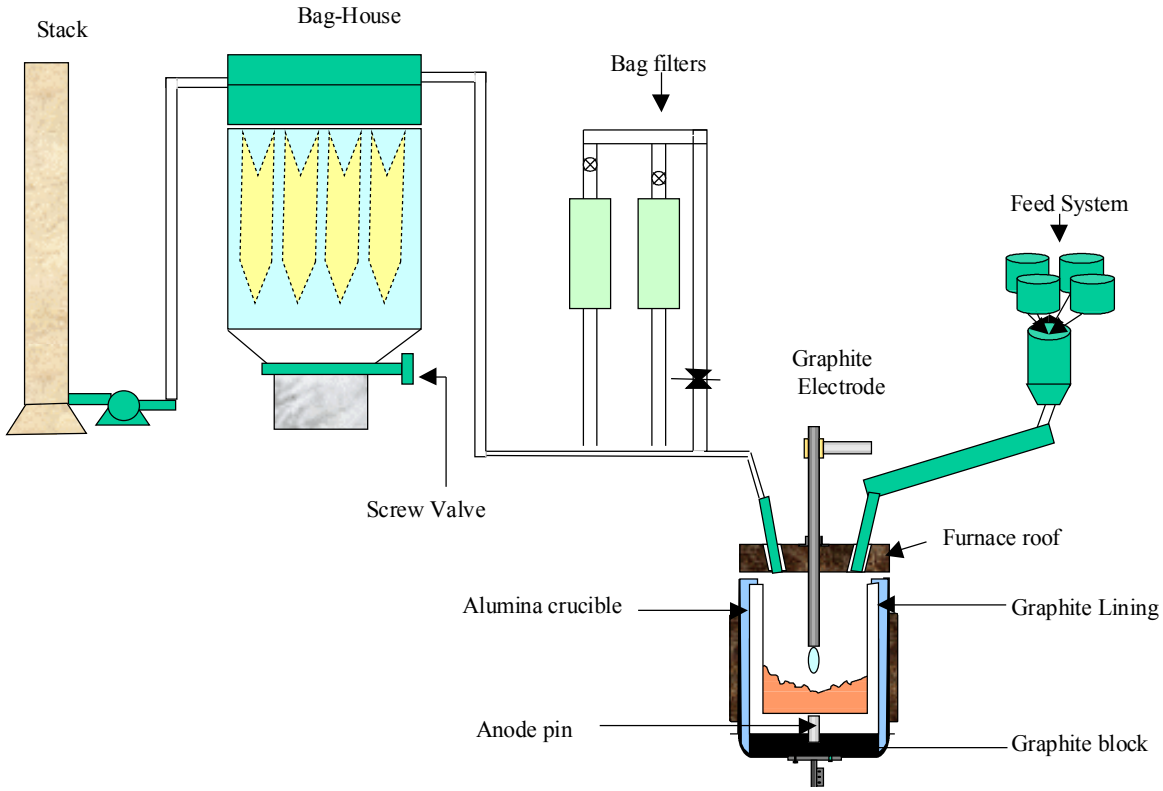

Figure 1. Schematic of the 100kVA facility.

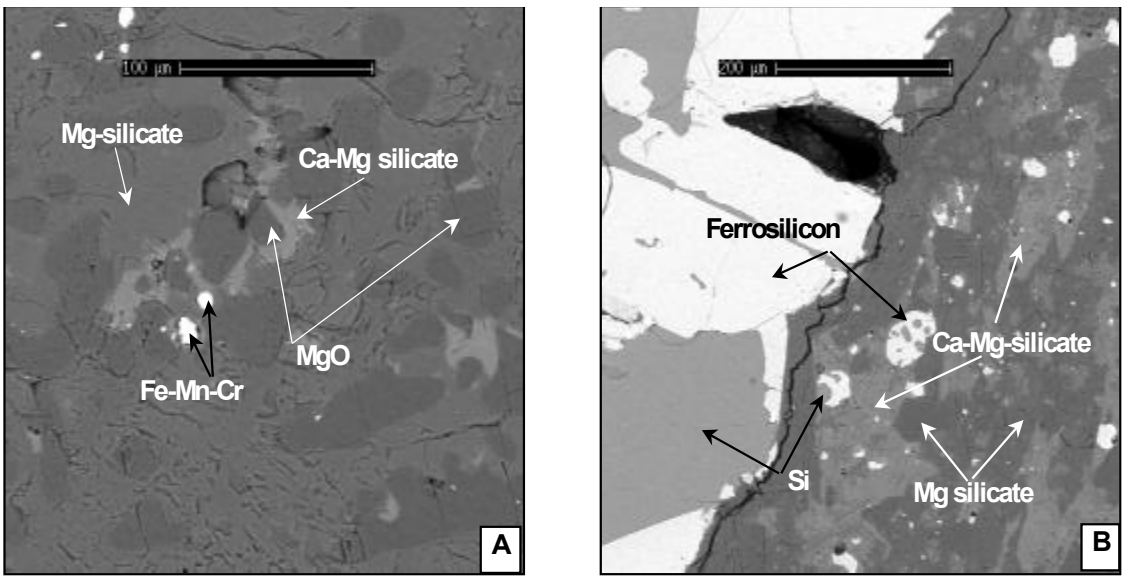

Figure 2: Back-scattered electron images of phases identified in the slags formed during Mg extraction from the magnesia-1.
A: Phases present in Slag Test 2. B: Phases present in Slag Test 4.

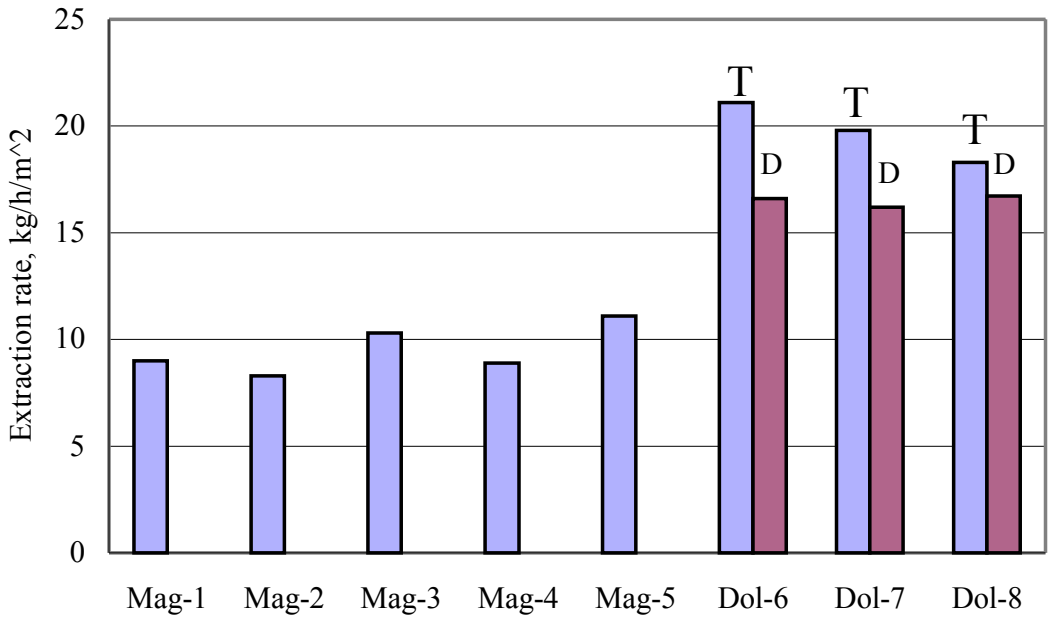

Figure 3. Average magnesium extraction rate (based on T: Tapped slag, D: Dig-out slag).