

Refining Testwork on Crude Magnesium Produced in the Mintek Thermal Magnesium Process

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Abstract - Samples of crude magnesium produced by the Mintek Thermal Magnesium Process were refined in two stages. The first stage consisted of co-melting of batches of the crude metal and $MgCl_2$ -KCl flux (cleaning), followed by stirring at 30 rpm for 30 minutes and settling of the sludge (mixture of molten salt and solid impurities) from the magnesium melt. The operating temperature was 680–730°C. Most of the contained calcium and significant proportions of iron and silicon were transferred into the sludge phase, which left a metal containing, on average, 950 ppm Si, 470 ppm Fe, and 230 ppm Ca.

In the second stage, small-scale refining tests were conducted on cleaned samples from the first stage, as well as on crude magnesium. $FeCl_3$ was used as the refining agent. These tests were carried out at 715–760°C with various amounts of the refining agent. The refined metal was suitable for the production of various magnesium alloys, particularly AZ91D.

INTRODUCTION

Thermal production of magnesium incorporates a refining stage whereby impurities in the condensed metal are removed with the help of certain salt fluxes. The major impurities that are commonly present include calcium, silicon, iron, and aluminium. These elements report to the crude metal in oxide and in metallic form. It is believed that these contaminants are generated by three main mechanisms¹. The first is related to particulate matter in the furnace feed that is entrained in the gas stream (mostly magnesium vapour) and settles inside the condenser. They include fine particles of calcined dolomite (dolime), ferrosilicon, and possibly aluminium. The second mechanism involves the physical and chemical interactions between the electric arc and the furnace bath. Physical interactions include the disintegration of feed particles as they are hit by the electric arc, which leads to the generation of micron-sized particles that are swept away with the gas stream into the condenser. Chemical interactions in the vicinity of the arc (the arc attachment zone, AAZ) produce certain sub-oxides, such as Al_2O and SiO . In addition, dissociation and vaporization of certain easily volatilized metals (Mn, Zn, etc.) could also take place in the AAZ. The metal sub-oxides can interact with the magnesium vapour as it cools down while flowing out of the furnace and into the condenser according to



Other possible reactions include



Clearly such reactions contribute to the contamination of the crude magnesium in two ways. First, by forming oxides of magnesium, aluminium and silicon, and secondly by adding to the metallic fraction of silicon and aluminium in magnesium metal. The third mechanism involves oxidation of magnesium vapour by –

1. Carbon monoxide (generated by the reduction of MgO with the graphite electrode and/or the carbon hearth refractories), and the subsequent reaction of magnesium vapour with carbon monoxide
2. Residual CO₂ in dolime
3. Air (air leaks)
4. Oxygen (from oxygen lancing to tap the slag)

Regardless of the nature of the contaminants or the mechanism that leads to their formation, the crude metal is usually contacted with various salt fluxes in order to purify it. This paper presents preliminary refining results obtained from the treatment of crude liquid-magnesium samples produced in the pilot plant of Mintek's Thermal Magnesium Process (MTMP) with MgCl₂-KCl, and subsequently with FeCl₃. This initial work represents an attempt to show that the MTMP crude metal has the potential to be purified so that, upon alloying, it can meet the AZ91D specifications.

METAL CLEANING WITH MgCl₂-KCl

Experimental Equipment

The testwork was done in the apparatus shown in Figure 1. It consisted of a 3Cr12 steel crucible, a heating system, and a stirrer assembly. The crucible had an ID of 1 m, a height of 1.7 m, and was made of 2-mm-thick plate. A tap-hole was located near the top of the dished bottom (250 mm from the base of the crucible). The crucible was covered with a mild-steel plate that was welded to the stirrer frame. An insulating board was located between the cover plate and the crucible. The cover plate contained an inspection port that was used to add the flux and to measure the bath temperature. The stirrer assembly consisted of an impeller (600 mm in diameter), a 50-mm-diameter mild-steel shaft, a 7.5-kW electric motor, a gearbox with variable-speed control (10–32 rpm), a fan to cool down the electric motor, and a mounting frame. The stirrer impeller was

designed to push the oxy-chlorides (sludge) downward onto the crucible base for effective separation of the magnesium from the sludge.

The crucible was placed inside a heat shield and was externally heated with a 2-GJ/h, or about 550-kW, propane burner. The crucible off-gas (mostly argon) was directed into a combustion chamber through a flexible steel duct, and then to a bag-house to capture any particulate matter entrained in the gas stream.

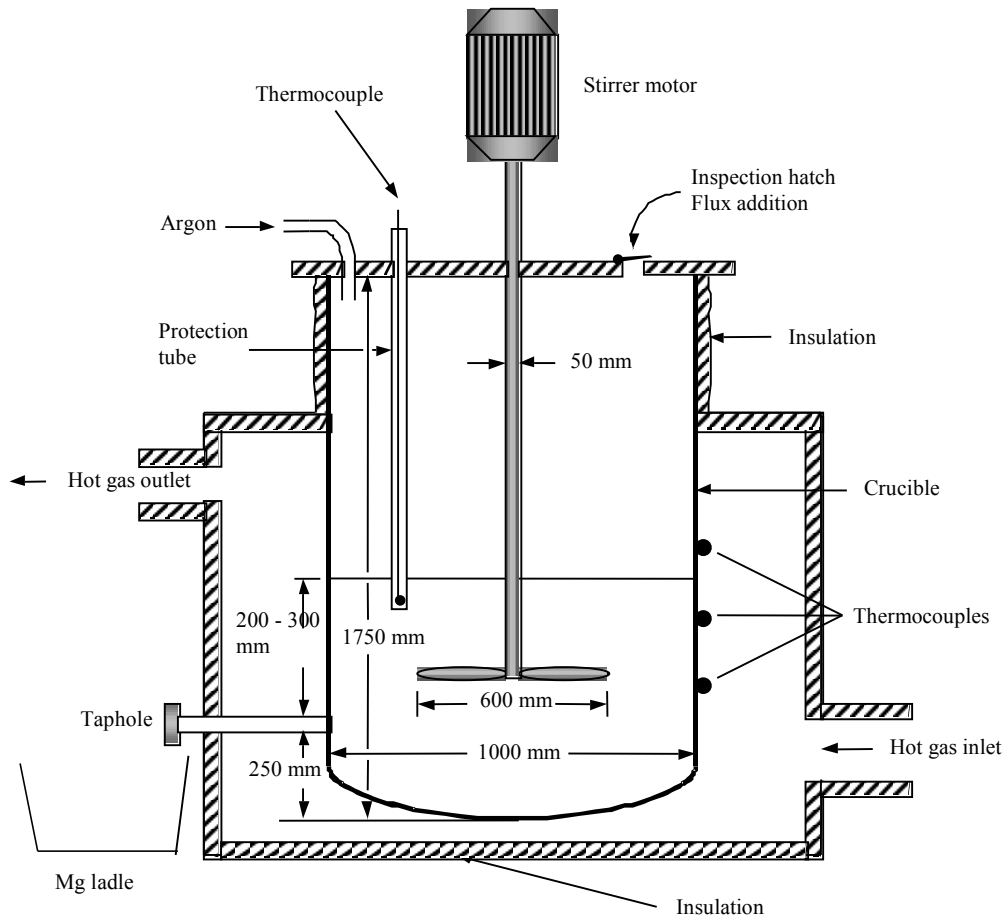


Figure 1: Schematic of the experimental set-up used for crude magnesium cleaning

Experimental Procedure

Batches of crude magnesium and fused salt consisting of magnesium and potassium chlorides (M130 flux) were charged into the crucible, melted and heated up to 680–730°C, as measured inside the crucible. The crude magnesium was produced in the MTMP pilot plant during November 2004³. Once the operating temperature was reached, the bath was agitated using the stirrer assembly for 30 minutes. The melt was then allowed to settle down for at least 20 minutes before it was tapped. In most taps, small amounts of fluorspar were added prior to the stirring period. Fluorspar is a coalescing agent for magnesium droplets that stick to the sludge. The stirrer speed used throughout the testwork was 30–32 rpm. Argon was used to maintain an inert atmosphere inside the crucible and thus to minimize magnesium oxidation. The argon flow rate was kept at 30–40 l/min (pressure set point of 40–60 kPa positive pressure),

except when magnesium burning was observed; it was then raised to 100 l/min. The combustion chamber pressure was adjusted to maintain a -2 to -5 mm H₂O negative pressure in the crucible, which prevented any gases/fumes from escaping into the workplace.

The cleaned metal was tapped into a 200-litre ladle, allowed to cool down and solidify, weighed and then separated from any sludge that came out with the magnesium metal and settled at the bottom of the tapping ladle. Small cup samples were taken from the magnesium stream and metal drill samples were prepared for later chemical analysis. In addition, 2–3 spoon samples (about 1.5 kg each) were also taken for later refining testwork with iron chloride. Sludge samples were also analysed after manually removing any trapped magnesium globules.

On average the batches carried 300 kg crude magnesium and 60 kg M130 flux. Small amount (2–13 kg) of fluorspar, a coalescing agent, was fed into the crucible just prior to switching on the stirrer. Smaller amounts of potassium chloride (0.5–1.0-kg batches) were charged into the crucible when magnesium burning was noticed. The average compositions of various fluxes used are shown in Table I.

Table I: Chemical analyses of the various fluxes, mass per cent

<i>Component</i>	<i>M130 Flux</i>	<i>Fluorspar</i>	<i>KCl</i>
Mg	9.69	NA	NA
Al	0.08	0.44	0.12
Si	0.37	0.215	0.94
Ca	2.13	48.45	0.019
Fe	0.20	0.236	0.03
Cl	56.15	0.0144	47.55
Na	NA	0.01	0.01
K	27.10	0.011	50.90
F	1.95	51.29	NA

NA: Not analysed

Results and discussion

Table II presents the average composition of the cleaned metal. For comparison purposes the chemical analysis of the crude magnesium is also included in the table, along with that of ASTM B92-grade 9980A. The deportment of major elements was calculated based on the recovered magnesium masses and analyses; it is presented in Table III. The figures suggest that most of the calcium originally contained in the crude metal was removed. It is believed that M130 flux acts in two ways in magnesium refining. First, it captures the oxide (and nitride) inclusions of Mg, Al, Ca, and Si, forming a heavy oxy-chloride phase called sludge, which settles out at the bottom of the refining crucible. Secondly, calcium present in metallic form is largely eliminated by a reaction with magnesium chloride:



Table II: Chemical analyses of crude and 'clean' magnesium, mass per cent

Element	ASTM B92 Grade 9980A	Crude Mg			Clean Mg		
		Avg.	Max	Min	Avg.	Max	Min
Al	0.05 max	0.066	0.210	0.010	0.040	0.235	0.003
Si	0.05 max	0.281	1.010	0.100	0.095	0.500	0.014
Ca	0.05 max	0.385	1.090	0.030	0.023	0.102	0.005
Fe	0.05 max	0.250	0.350	0.002	0.047	0.100	0.002

Table III: Department of aluminium, calcium, iron, and silicon, mass per cent

<i>Element</i>	<i>Clean Mg</i>	<i>Dross</i>
Al	55	45
Ca	3	97
Fe	17	83
Si	34	66

Although it was not possible to determine the relative proportions of calcium present as metal, previous testwork indicated that when the crude magnesium was co-melted with a NaCl-KCl mixture, about 50–60% of the total calcium originally present reported to the sludge phase, an outcome that suggests that 40–50% of the contained calcium was in metallic form.

The results also indicate that a large proportion of the silicon reported to the dross phase, which suggests that less than 34% of the original Si content was present in a metallic form. In addition, about 45% of the aluminium was removed from the crude metal during the cleaning stage. These results are in agreement with those reported in the literature^{1,2}.

Although the M130 flux is believed to be ineffective in removing the iron in magnesium metal, the calculated results show that most of the iron was transferred to the dross phase, which is possible if the iron was originally in the form of oxides. In addition, reduction of iron oxide by magnesium and the subsequent settling of the metallic iron could have contributed to the high Fe-department to the sludge phase.

Table IV presents the average sludge composition. In certain taps the dross contained small magnesium globules that could not easily be separated prior to running the chemical analysis. This may have resulted in relatively high levels of magnesium in certain dross samples. The use of aluminium trifluoride instead of fluorspar could lead to better metal-dross separation, and thus lower losses of the metal. Operating at higher temperatures could also assist in increasing the metal recovery.

Table IV: Average chemical analyses of the dross

<i>Component</i>	<i>Mass %</i>	<i>Component</i>	<i>Mass %</i>
Mg	17.39	Cl	38.61
Al	0.46	F	3.44
Si	0.30	K	14.02
Ca	3.59	Na	0.43
Fe	0.18	N	0.57

Balance mostly oxygen with minor amounts of Cr, Mn, Ti

In total about 4.2 tons of crude magnesium were processed during the test, which gave a recovery of about 3.8 tons of “cleaned” metal. Based on the amount of flux used and the mass of the dross generated, flux consumption was about 2 kg/1 kg of oxides/solids initially present in the crude magnesium. However, the flux consumption was as low as 1kg/kg of oxides in certain taps.

The magnesium mass balance and its chemical analysis indicated that the metallic losses to the sludge phase were about 9%. This is in comparison to 5-8% losses in the refining-cleaning stage of the Magnetherm process.

REFINING WITH FeCl₃

Experimental equipment

A schematic of the apparatus used for the refining testwork is shown in Figure 2. It consisted of an electric-resistance heating furnace, a 3Cr12 steel crucible, and stirrer assembly. The crucible had an ID of 130 mm at the base and 150 mm at the top, with a height of about 180 mm. The crucible lid was made of 8-mm mild-steel plate and contained entry ports for the stirrer shaft, the thermocouple, the FeCl₃ feed port, and sampling port. The crucible temperature was controlled with the thermocouple located at its exterior sidewall. The set-point was adjusted to give a magnesium bath temperature of 710–760°C. The stirrer impeller was designed to force the solids to the bottom of the crucible. The stirrer was provided with a variable speed motor.

Experimental procedure

The procedure used in the refining stage was as follows: about 1800 g of magnesium lumps (obtained from the cleaning tests) were added to a crucible along with 50 g of M130 flux (as cover flux); a flow SF₆ (2% SF₆, 98% air) was introduced to prevent the oxidation of the molten magnesium. The heating system was turned on to melt the charge and to raise the bath temperature to the desired value. Once the bath was fully molten, a supply of argon was introduced and the SF₆ flow switch off. This was done to prevent the oxidation of molten magnesium with air contained in the SF₆. The stirrer was then turned on to the desired speed, followed by the addition of a certain proportion of the required FeCl₃. After the stirrer had run for a specified period, it was turned off and the bath allowed to settle for 10–20 minutes. A sample was then taken for chemical analysis. The procedure was repeated until all the FeCl₃ had been

added. Table V gives the details of the test conditions, whereas Table VI presents the chemical analyses of the clean magnesium samples used in each test. For comparison, the analysis of magnesium alloy AZ91D is also included in the table.

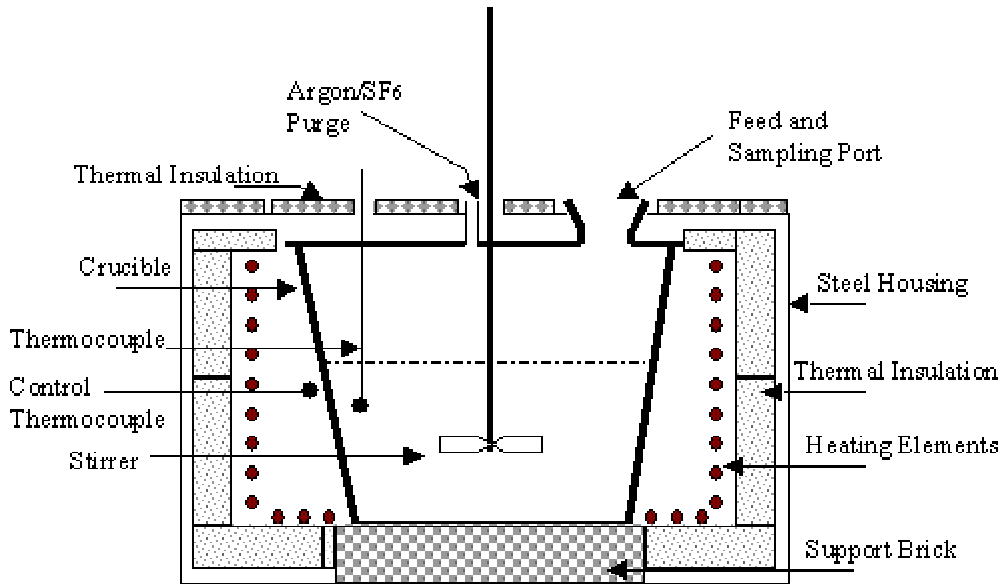


Figure 2: Schematic of the experimental set-up used for FeCl_3 refining

Table V: FeCl_3 refining-experimental conditions

Test No.	Mg, g	M130, g	FeCl_3^4 , g	Bath temp., °C	Stirrer, rpm	Stirring time ¹ , min	Settling time ¹ , min
Ref-1	1814.7	50	52.2 (3)	730	30	20	10
Ref-2	1794.6	50	52.2 (3)	729	50	20	10
Ref-3	1800.9	50	32.3 (3)	716	30	20	20
Ref-4	1795.1	50	11.8 (3)	722	30	20	20
Ref-5	1810.3	50	10.6 (2)	723	30	30	20
Ref-6	1827.3	50	72.7 (3)	726	30	30	20
Ref-7 ²	1821.3	50	84.3 (3)	727	30	30	20
Ref-8 ³	1800.2	180	100.2 (4)	720	30	30	20
Ref-9 ³	1777	180	50.2 (2)	759	30	30	20

1: Indicated times refer to the stirring and settling periods after the addition of a given FeCl_3 batch

2: Refined magnesium from refining Tests 1 and 2

3: Crude magnesium

4: Number in brackets indicates the number of FeCl_3 batches.

Table VI: Chemical analyses of the starting magnesium samples and AZ91D alloy, mass per cent

Component	Ref-1	Ref-2	Ref-3	Ref-4	Ref-5	Ref-6	Ref-7	Ref-8	Ref-9	AZ91D
Al	0.878	0.878	0.448	0.207	0.057	0.041	0.083	0.095	0.145	8.5-9.5
Ca	0.102	0.102	0.013	0.025	0.088	0.023	0.056	0.084	0.084	0.010
Si	0.518	0.518	0.263	0.111	0.099	0.104	0.120	0.097	0.097	0.080
Fe	0.125	0.125	0.050	0.026	0.030	0.030	0.042	0.029	0.029	0.004

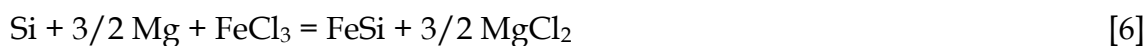
In Test 7, the products of Tests 1 and 2, having similar silicon contents, were used in attempt to lower Si compositions to <0.08%. In addition, Tests 8–9 used crude magnesium samples, and therefore the M130 flux addition was increased to 180 g, or 10% of the mass of the crude magnesium. These two tests aimed at simulating an industrial refining process, where the various fluxing agents would be charged sequentially. In tests 9, fluorspar was added as a coalescing agent.

Results and discussion

The cleaned metal samples used in this testwork were selected on their relatively high silicon content. As such, these samples represented the worst case in refining requirements. Note that most of the cleaned metal contained <0.05% Si³, and that only a few batches were high in silicon.

For most of the tests conducted, the silicon content of the refined magnesium tended to drop rapidly after adding the first batch of ferric chloride (Figure 3), beyond which further additions of the refining agent did not improve the metal quality significantly. This was more evident when treating cleaned magnesium samples that contained more than 0.26% Si. It seems that the lower the Si content of the treated sample the more difficult it is to bring it down further, even with increased and progressive additions of FeCl₃. Also, in certain tests, the silicon content tended to increase with the addition of later batches of ferric chloride. This behaviour is not well understood, but sampling and analytical errors cannot be ruled out. Note that similar behaviour was reported earlier².

In Tests 1 to 5, ferric chloride additions were based on the following reaction:



where three times the stoichiometric amount was charged in three equal batches, except in Tests 5 and 9, where FeCl₃ was added in two batches, at equal time periods (see Figure 3 for details of timing of FeCl₃ additions, stirring, settling, and sampling for a given test). As reaction 6 suggests, the role of ferric chloride is to capture the dissolved silicon and convert it into an FeSi alloy, which settles out along with any chloride/oxy-chloride phase, thereby forming a heavy sludge layer at the bottom of the crucible. In other words, this refining step aims at minimizing the silicon composition in the magnesium metal, but it does not contribute appreciably to the lowering of other metallic impurities, such as Fe, Mn, Cr, Ni, and Al.

In Tests 1 and 2 (Figure 3), the final silicon content in the refined metal did not drop to below the target value of 0.08% (AZ91D specification), although 75–84% of the contained silicon was removed. Increasing the stirrer speed to 50 rpm (Test 2) appeared to have decreased the silicon content in the final metal, but not to below the target level. Further increase in the stirrer speed was not considered because of the burning of magnesium metal during Test 2, and therefore the other tests were carried out at a lower stirrer speed of 30 rpm. Giving the refined metal more settling time did not result in a decrease in the final Si content, which remained at 0.095% for both Tests 3 and 4 (Figure 4). In addition, increasing the stirring period to 30 minutes (Test 5, Figure 5), as opposed to 20 minutes previously, did not appear to improve the metal quality.

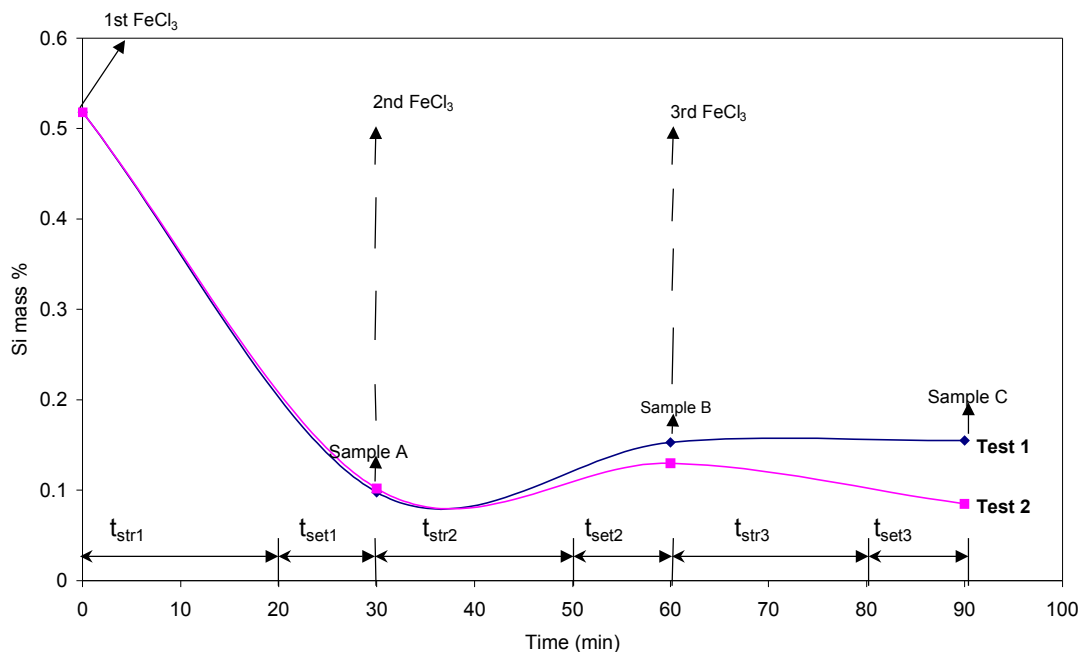


Figure 3: Silicon analyses versus time.^{1,2} (t_{str} refers to stirring period, and t_{set} indicates settling period)

These results suggested that changing the stirrer speed, settling period, or the stirring time did not produce a final metal containing less than 0.08% Si. In addition, visual examination of the samples taken indicated the presence of certain impurity inclusions, which tended to be more abundant and visible towards the bottom of a sample. Chemical analyses conducted on both the top and middle sections of certain samples tended to show that the top layer contained less silicon (and to a lesser extent, other impurities) than the middle section (Figure 6).

The above two considerations led to the revising of the test programme, where in Tests 6–9 $FeCl_3$ addition was increased beyond the calculated values of reaction 6. In addition, fluorspar was added in Tests 9 in order to evaluate the influence of a coalescing agent on the settling behaviour of $FeSi$ and other reaction products. As one can see in Figure 5, increased additions of $FeCl_3$

produced a refined metal containing 0.064–0.072% Si (Tests 6–7). This corresponded to a removal of about 32–50% silicon.

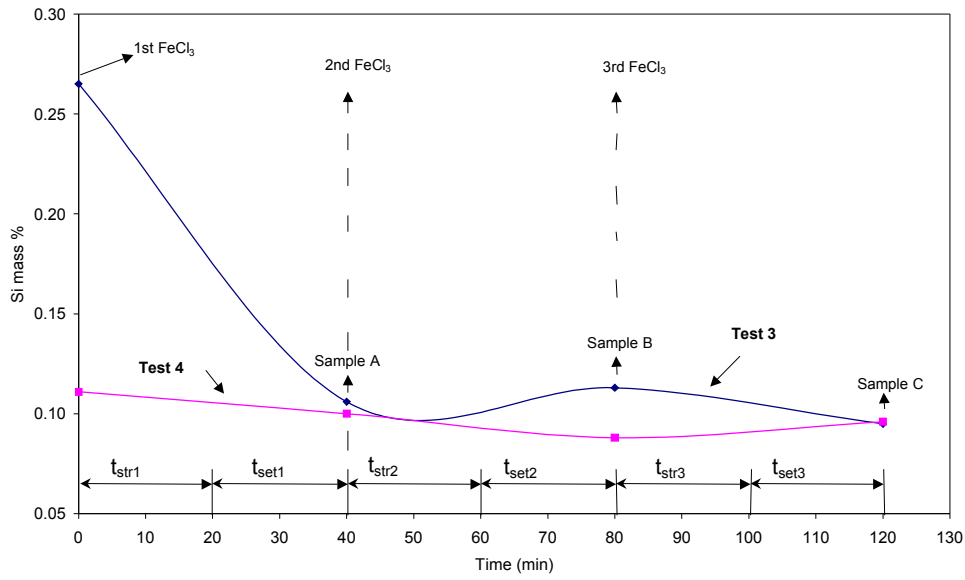


Figure 4: Silicon analysis versus time^{3,4}

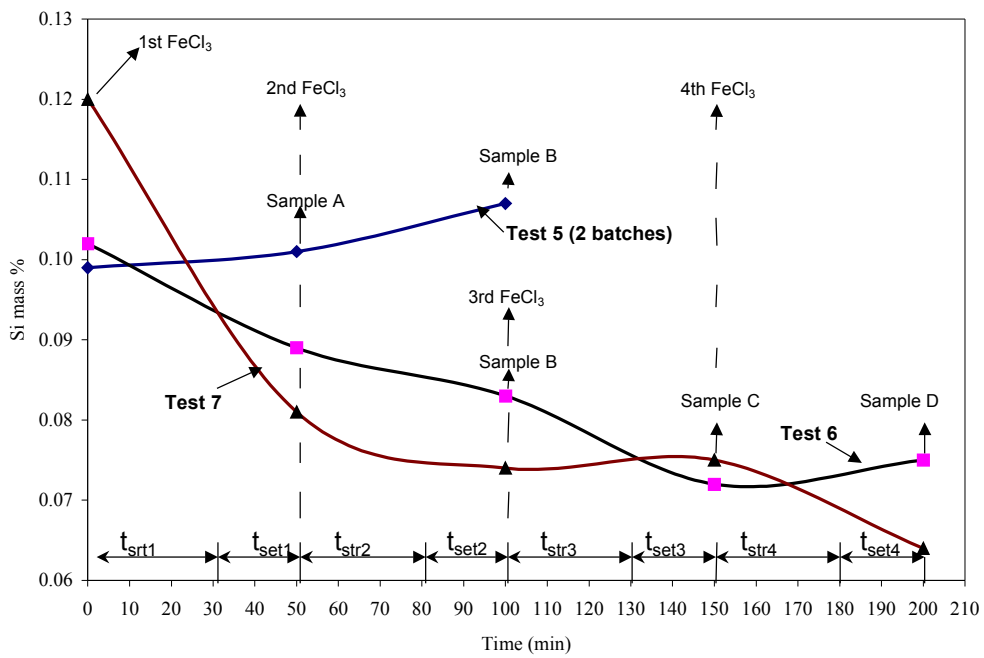


Figure 5: Silicon analysis versus time^{5,6,7}

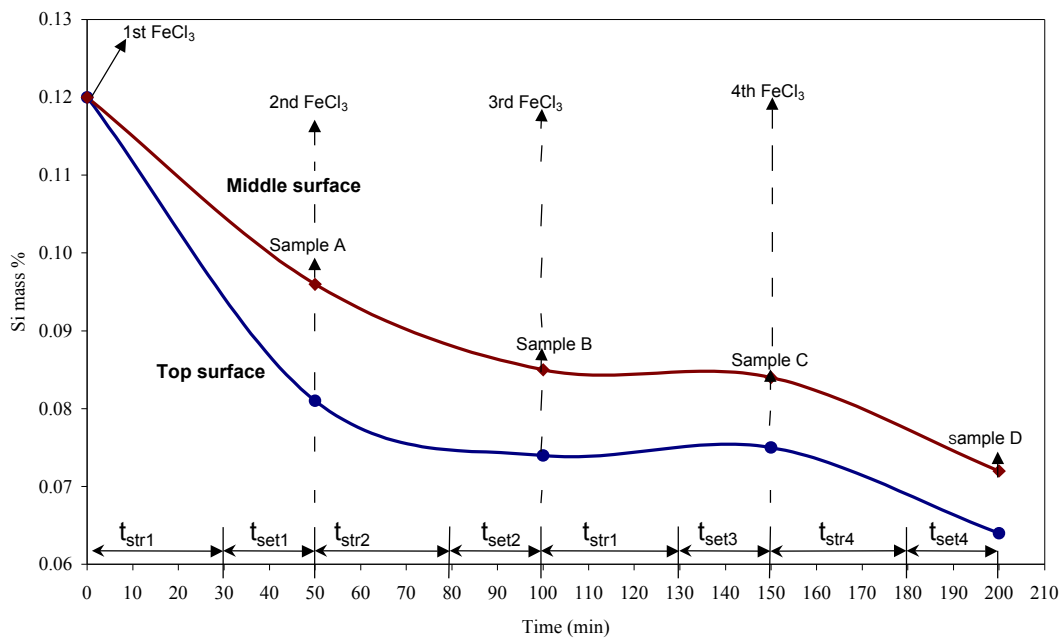


Figure 6: Variation in silicon analysis between top and middle surfaces in the refined metal versus time⁷

Carrying out the refining work immediately after the cleaning step with the appropriate amount of M130 flux (Test 8) produced a final metal containing about 0.064% Si (Figure 7). This is very similar to the results obtained in Test 7, and suggests that the metal quality (in terms of Si-content) is not affected to any appreciable degree whether the FeCl_3 refining is performed immediately after metal cleaning, or after the clean metal has been allowed to cool and solidify.

Test 9 conditions were similar to those of Test 8 except that fluorspar (10 g) was charged into the crucible as a coalescing agent with the first batch of ferric chloride (only two FeCl_3 batches were added), and the bath temperature was raised to 760°C . As Figure 7 indicates, in Test 9 the silicon content was lower than that of Test 8. This is believed to be related to the combined effect of increased temperature and the presence of fluorspar, where the metal viscosity and the surface tension between the dross (including FeSi globules) and magnesium metal are both decreased, which allows better separation and faster settling of the reaction products.

It should be noted that the above refining work did not have any major influence on the analysis of iron, manganese, and nickel. Also, the aluminium content in the refined magnesium did not change during refining, except when fluorspar was employed as a coalescing agent, when it increased slightly. Similar observations were made when the crude magnesium was co-melted with M130 flux in the presence of fluorspar. On the other hand, the calcium content was consistently lower in the refined metal compared with the clean samples. This is believed to be related to the addition of small amounts of M130 flux at the beginning of each test.

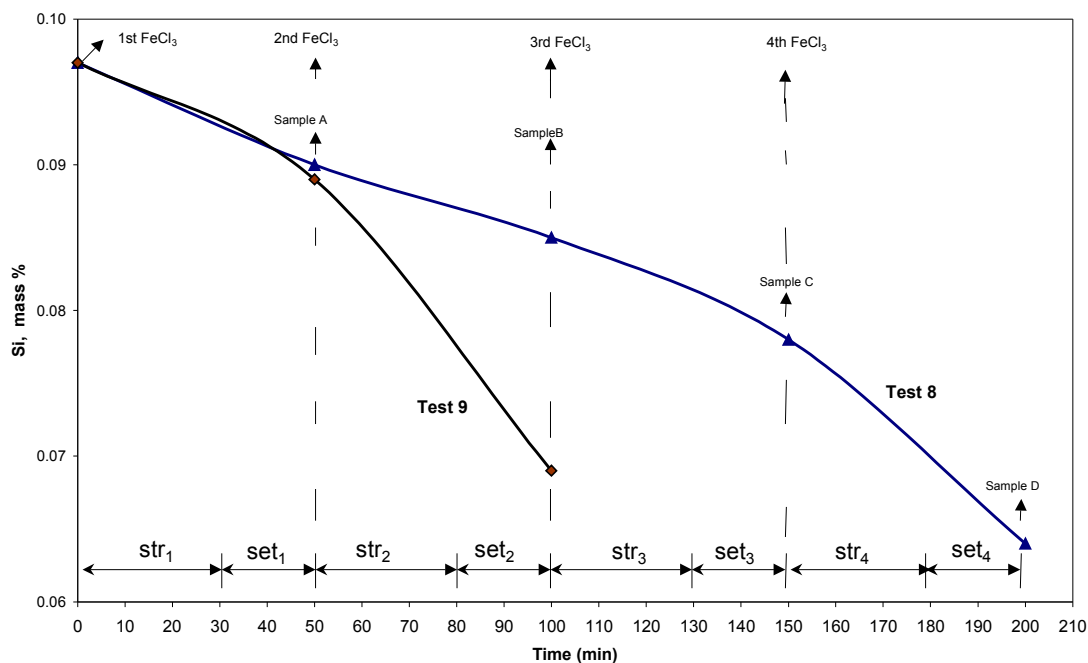


Figure 7: Silicon analysis versus time^{8,9}

Figure 8 presents the initial rate of silicon removal as a function of the silicon analysis in the clean magnesium samples used in Tests 1–8; it excludes the data of Test 5. The initial rates were calculated based on the silicon content of the magnesium samples taken at the end of the first stirring-settling period and that of the starting material. In addition, the reaction time refers only to the stirring period after the addition of the first batch of FeCl₃. Note that for the indicated tests the operating temperature was 616–730°C. As the graph shows, there is a good linear correlation between the calculated rates and the silicon content of the starting samples of magnesium. The relationship can be represented as

$$\text{Rate (g/min)} = 0.89 \times (\text{mass \% Si}) - 0.85$$

The relationship suggests that the initial rate is first order with respect to silicon content, and that the reaction might be reversible.

CONCLUSIONS

Crude magnesium samples produced in the Mintek Thermal Magnesium Process were refined in two steps. In the first step, co-melting the crude metal with fused MgCl₂-KCl flux produced an oxide-free (clean) magnesium. The clean metal contained, on average, 950 ppm Si, 470 ppm Fe, and 230 ppm Ca.

In the second, or refining, step small clean samples were treated with anhydrous ferric chloride in order to lower the silicon content. The variables investigated included agitation speed (rpm), stirring time, settling period, FeCl₃ addition, temperature, and the addition of fluorspar as a coalescing agent.

Chemical analyses of the refined metal show that, upon alloying, the metal can conform to the standards of various magnesium alloys, particularly those of the AZ91D die-casting alloy.

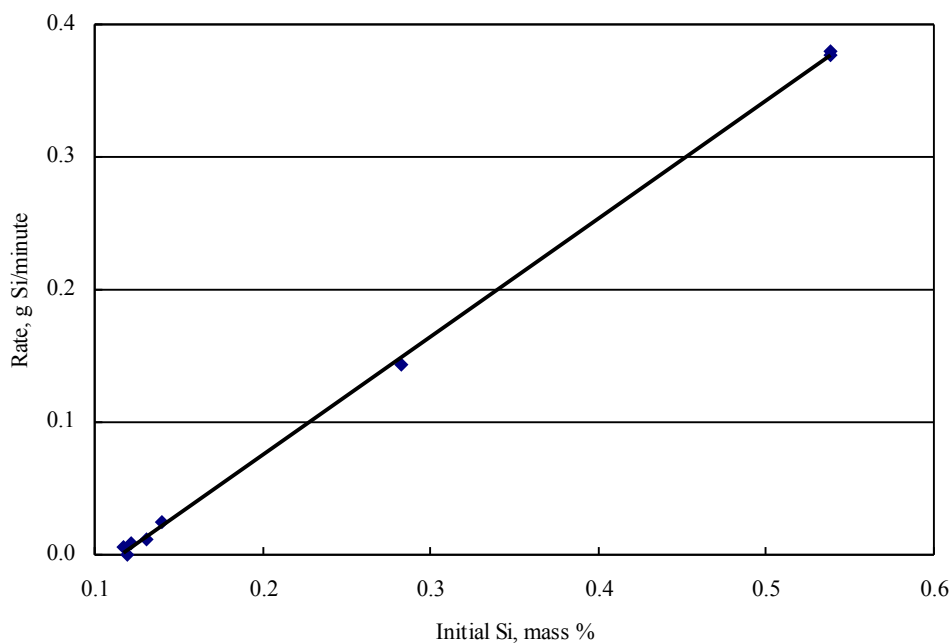


Figure 8: Initial silicon removal rate versus the silicon analysis in the clean metal

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