XRF’S ROLE IN THE PRODUCTION OF MAGNESIUM METAL BY THE MAGNETHERMIC METHOD

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ABSTRACT

X-ray fluorescence has been the major analytical tool used at Northwest Alloys for the production of magnesium since our startup 24 years ago. In this paper I will give a brief outline of the production process presently being used at Northwest alloys and review the quantitative analysis being performed by XRF and the specimen preparation techniques being used. Finally, I will discuss how the qualitative XRF scans have helped us to solve problems that have risen from time to time.

INTRODUCTION

Northwest Alloys is a subsidiary of Alcoa and has been producing magnesium since early 1976. We employ a process that is a modification of the magnetherm process developed by Pechiney. In the magnetherm process we operate a reduction furnace at 70 Torr pressure and use thermal decomposition to convert magnesium oxide to magnesium. Aluminum and 75% ferrosilicon are used as reductants in the process. See Figure 1.

XRF was chosen as the main analytical tool because of its ability to analyze many different types of samples with several different types of specimen preparation. At Northwest Alloys we employ many of the specimen preparation techniques available for XRF with the exception of liquid analysis. We have seen several changes in both instrumentation and specimen preparation equipment over the years. As computers have advanced we have gone from a basic “modified delta” matrix correction developed by Charles Matucha [1] at the Alcoa Technical Center to the more advanced fundamental parameter procedures utilized by equipment manufacturers today.

SPECIMEN PREPARATION TECHNIQUES

Pressed Pellets

Our pressed pellet technique has evolved over time. In the original procedure the sample was ground in a slurry with freon and a binder. This procedure was discontinued due to the cost and availability of freon. In our present method a 10 gram sample is ground with 0.6 grams of binder. This procedure was initially set up for ferrosilicon with the help of Torkild Eivindson from Elkem Research [2]. The procedure has since been adapted to several other types of materials with good success. This procedure yields a strong specimen with a good flat surface ready for XRF analysis.
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Figure 1
Fused Beads

The fused bead technique we employ uses lithium tetraborate in a 6:1 ratio with the sample. Unlike some fusion techniques that predry the flux and perform a Loss On Ignition of the sample before making the fused bead [4], we make a blank bead using our specimen preparation procedure. From the moisture/volatile loss of the flux we calculate a “Fused Flux Factor” and use this factor in the following equation to obtain a “Loss of Fusion” value for the specimen.

$$100-\frac{\text{[Final Bead Weight]}-(\text{[Weight of Flux]} \times \text{[Fused Flux Factor]})}{\text{[Sample Weight]}} \times 100$$

The “Fused Flux Factor” is a percentage of the flux after it is fused into a bead. The “Loss of Fusion” value compares well with the standard “Loss on Ignition” value, and has the advantage of eliminating one step in the sample preparation process.

From 1974 to 1995 Northwest Alloys used an automatic fusion device developed at the Alcoa Technical Center [3] [4], which allowed the bead to be cast directly in the crucible. This technique worked fine until a change in the chemistry of the furnaces caused a high iron non-magnetic ferrosilicon material to be left in the slag. This material damaged the platinum crucibles used in the analytical process. At the present time Northwest Alloys has discontinued using platinum crucibles for slag fusion and is now using a graphite crucible in a muffle oven. This manual technique provides the information that is needed to control the chemistry in the reduction furnaces without the high cost of platinum crucibles. This fusion technique is also used in all of our fused bead procedures. The surface of the bead as it comes out of the graphite crucible is not suitable for XRF analysis. We must polish the bead using a 30 micron bonded diamond polishing disk and water to get a surface that is suitable for XRF analysis.

Machined Metals

Metals are the easiest of all our samples to prepare. Both the magnesium and aluminum samples are milled on a small vertical mill to a constant height. The inside of the mill is flooded with argon to eliminate any chance of motor sparks igniting the magnesium fines. This mill gives a nice smooth flat surface suitable for XRF analysis without further polishing.

APPLICATION OF THE PREPARATION TECHNIQUES

Raw Materials

Dolomite

The dolomite ore, which is the main source of magnesium for our process, is mined on site. The ore is analyzed as exploration drillings and final crushed sized product. The use of the pressed pellet or fused bead preparation technique is dependent upon the sample type.

Drill samples taken during the mapping of the quarry only require Pb and SiO$_2$ analysis for quality control of the mine. We employ the pressed pellet technique for drill samples to allow preparation of a large number of samples in a short amount of time. In this analysis we are only looking at two elements that constitute a small fraction of the elements present and do not use the fundamental parameter approach for matrix corrections. Instead we use regression curves.
without matrix corrections. This works well because our mine is fairly consistent and any large deviation from the norm indicates an area we will not mine.

The other place where the dolomite ore is sampled is during the crushing and sizing process. Here we apply both the pressed pellet and the fused bead techniques. During the crushing operation composite samples are made every hour. An analysis of Pb and SiO$_2$ for quality control is needed as fast as possible. We quickly make a press pellet and run this on the XRF. We also retain a small amount of the original sample and make a daily composite of the hourly samples. This composite is ground to a –100 mesh, blended, and then prepared as a fused bead following our standard procedure. This specimen is then analyzed by XRF for the complete chemistry shown in Table 1.

Calcined Dolomite (Dolime)

Northwest Alloys' reduction furnaces operate at 70 Torr and the dolomite must be calcined to remove the CO$_2$ before the dolomite is introduced into the furnace. The CO$_2$ is removed in a rotary limekiln with a hot zone temperature of 1450$^\circ$C. Samples are taken every 6 hours to check the surface area of the calcined material. The surface area provides a direct indication of the burn efficiency of the kiln. We also utilize this sample to make a press pellet for a quick analysis of the Pb and SiO$_2$ levels of the product to ensure there is no segregation in the kiln. Similar to the dolomite crusher samples, we retain a small amount of the original sample and at the end of a 24 hour period, we make a composite, grind it to a –100 mesh, blend and prepare a fused bead following our standard procedure. This specimen is also analyzed by XRF for the complete chemistry shown in Table 1.

Ferrosilicon

Ferrosilicon is our main reductant in the production of magnesium from magnesium oxide. We are currently using a particle material from Elkem that is 75% Si. We utilize the pressed pellet technique for the specimen preparation of this material. Working with Elkem [2] we developed a procedure that provides close correlation between the supplier's and customer's analytical results.

Magnesite

The magnesite in our process provides additional magnesium units to the reduction furnaces. We have established two different procedures for analysis of this material. Preparation of a fused bead was the original method for specimen preparation. We had to deviate from our standard 6:1 flux:sample ratio and use a 12:1 ratio in order to get the magnesium oxide to go into solution and form a good bead. This worked well until the level of detection requirement for Pb was reduced to less than 10 PPM. Currently we are using a pressed pellet technique modeled after our ferrosilicon procedure that allows us to analyze for the low levels of Pb.
Aluminum

Aluminum metal in the form of shot is also used as a reductant in the process. The resulting aluminum oxide that is formed in the slag acts to fluidize the slag and makes tapping the furnaces easier. Since the material we use comes in shot form we remelt a sample in a muffle furnace and pour the molten material into a mold to get our specimen. This specimen is then surfaced using the laboratory milling machine and analyzed by XRF.

**Process Samples**

**Furnace Slag**

During a production cycle the magnesium furnaces must be tapped twice to remove the excess slag. At each of these taps a sample of the slag is captured and sent to the Lab for analysis. Our slag is primarily dicalcium silicate that changes phases as it cools and decrepitates into a 100-200-mesh powder. Initial sample preparation requires cooling, screening the material through a 100-mesh screen and removing as much of the magnetic residual ferrosilicon as possible. The resulting sample is fused using our standard fusion technique to produce a glass bead that is then analyzed by XRF.

**Residual Ferrosilicon**

The iron content of the ferrosilicon that is added to the process is not consumed in the production of magnesium and is tapped out with the slag. The “residual ferrosilicon” that is tapped out has the composition of 70-75% Fe and 25-30% Si. As the silicon content of the residual ferrosilicon material approaches 30% the material becomes less magnetic, making it harder to separate it from the slag.

We currently do not analyze the residual ferrosilicon on a regular basis but we have procedures in place that allows us to do so if needed. The procedure is to make a press pellet specimen from the material following basically the same procedure for the ferrosilicon, but the sample:binder ratio is changed to 15:0.2. The procedure change is due to the density difference in the two types of ferrosilicon materials. When we attempted to use the standard 10:0.6 sample:binder ratio for the residual ferrosilicon we found that the sample would stick in the grinding dish and did not produce a very uniform specimen. By increasing the sample:binder ratio we were able to get a good specimen for XRF analysis.

**Final Products**

**Magnesium**

All of our magnesium, both pure and alloy are handled in the same manner. The specimens are received from the cast house, milled to a consistent depth, and analyzed on the XRF. XRF analysis could not be used for measuring the 5-10 PPM beryllium that is added to the alloys. Initially we turned to our ICP for this analysis but have recently purchased an OE spark unit for our metal analysis.
**Table 1**

<table>
<thead>
<tr>
<th>Material</th>
<th>Preparation</th>
<th>Elements Analyzed</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dolomite</td>
<td>Fusion</td>
<td>Fe₂O₃, MnO, SiO₂, Al₂O₃, P₂O₅, MgO, Na₂O, TiO₂, CaO, K₂O, SO₃</td>
</tr>
<tr>
<td></td>
<td>Pressed Pellet</td>
<td>Pb, SiO₂</td>
</tr>
<tr>
<td>Calcined Dolomite</td>
<td>Fusion</td>
<td>Fe₂O₃, MnO, SiO₂, Al₂O₃, P₂O₅, MgO, Na₂O, TiO₂, CaO, K₂O, SO₃</td>
</tr>
<tr>
<td></td>
<td>Pressed Pellet</td>
<td>Pb, SiO₂</td>
</tr>
<tr>
<td>Ferrosilicon</td>
<td>Pressed Pellet</td>
<td>Pb, Zn, Cu, Ni, Fe, Mn, Si, Al, P, Ti, Ca</td>
</tr>
<tr>
<td>Magnesite</td>
<td>Fusion</td>
<td>Fe₂O₃, MnO, SiO₂, Al₂O₃, P₂O₅, MgO, Na₂O, TiO₂, CaO, K₂O, SO₃</td>
</tr>
<tr>
<td></td>
<td>Pressed Pellet</td>
<td>Fe₂O₃, MnO, SiO₂, Al₂O₃, P₂O₅, MgO, Na₂O, TiO₂, CaO, K₂O, SO₃, Pb</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Metal</td>
<td>Pb, Zn, Cu, Ni, Fe, Mn, Si, Mg, Ti, Sn</td>
</tr>
<tr>
<td>Furnace Slag</td>
<td>Fusion</td>
<td>Fe₂O₃, MnO, SiO₂, Al₂O₃, P₂O₅, MgO, Na₂O, TiO₂, CaO, K₂O, SO₃</td>
</tr>
<tr>
<td>Residual Ferrosilicon</td>
<td>Pressed Pellet</td>
<td>Cu, Ni, Fe, Mn, Si, Al, Ti, Ca, Mg</td>
</tr>
<tr>
<td>Magnesium-Pure</td>
<td>Metal</td>
<td>Pb, Zn, Cu, Ni, Fe, Mn, Si, Al, Na, Ca, Sn, Ti</td>
</tr>
<tr>
<td>Magnesium-Alloy</td>
<td>Metal</td>
<td>Pb, Zn, Cu, Ni, Fe, Mn, Si, Al, Ca, Sn, Ti</td>
</tr>
</tbody>
</table>

**OTHER APPLICATIONS FOR XRF**

The ability to do a qualitative scan across the whole periodic table has at times provided us a wealth of information very quickly. This technique has provided an easy way to check for other contaminate that we normally do not look at in our raw materials. This is especially useful when we are evaluating a new supply source. We have also used this technique to trace down problems that occur in the operation of the furnaces. We have had several successes where the scanning technique has given us an answer and shown the direction we need to proceed in a matter of minutes. Wet chemistry techniques would have required hours or days of analytical work.

**CONCLUSIONS**

For the Lab at Northwest Alloys, the XRF has proven to be a very good choice for primary analytical instrumentation. The specimen preparation procedures are simple and reproducible. Ease of operation of the instruments and time required for analysis is very acceptable. With the use of the XRF we have been able to keep manpower to a minimum while turning out good reliable analysis with shorter turn around times when compared to most wet chemistry methods.
REFERENCES


