Analytical Challenges in Refractory Materials

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I have been involved in the refractory industry for many years and at some time or another I have designed materials, tested materials, manufactured materials, installed materials, in fact I have done everything except actually chemically analyzed a refractory material.

So I would not even begin to tell you how to analyse a refractory material. I'm sure everyone here knows more about chemical analysis than I do.

However you could regard me as a customer with and perhaps the insights I have developed may help in putting the role of chemical analysis in the Refractories into perspective.

For a start, let's take a step back and ask why we test refractories. The refractories handbook of the American Foundry Association gives four reasons:

1. To determine appropriate specification.
2. For quality control, to ensure conformance to specifications.
3. To provide special property information not available elsewhere.
4. For postmortem analysis to determine property changes in service and provide information that can point the way to better service.

I want to discuss these points with regard to the role of chemical analysis and in particular the abuse of in house chemical analysis facilities.

Let me talk first about determining appropriate specifications. Most refractory products are made from alumino-silicate raw materials.

The phase diagram for alumino and silica is as follows:

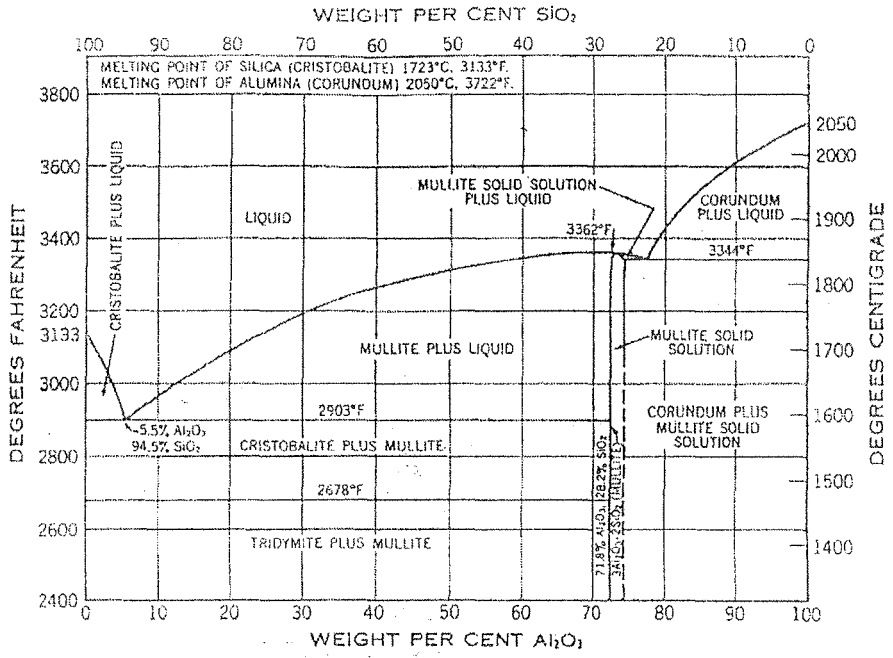

FIG. 2-1. Equilibrium diagram of the system alumina-silica (Al_2O_3-SiO_2). After Aramaki and Roy (Nature, August 1959)

In South Africa the two major refractory raw materials are calcined clay (about 44% Al2O3) and andalusite (about 59% Alumina).

Both of the large companies I worked for mined their own raw materials and so we needed a specification.

Those who understand phase diagrams will realize that at about 44% alumina small changes in alumina content make very little difference – but we nonetheless insisted on having a rigid specification. We draw an arbitary line in the sand and everything on one side was ok and the other regret.

As far as andalusite was concerned one of our customers gave us a specification for an andalusite brick.

Iron had to be less than 0.8%.

According to the customer bricks with 0.9% iron didn't work. Surprising since the iron occurred in small local spots and wasn't distributed through the brick.

Some years later it became apparent that this specification was designed to force us to buy andalusite from a specific quarry and that the customer had a relationship with the owner.

This forced us to chemically check all our raw materials and product. Thus the analyst was running hundred of analysis for a political purpose that had very little technical basis.

Many of the other specifications were similarly arbitary but one established became law and we rigorously tested material to ensure that they conformed.

Testing for conformance to specification is equally abused. An example was the testing of our clays.

In a clay quarry we first drilled cores and analyzed them so we knew the analysis of various parts of the quarry.

Then we tested every 100 tons mined (how do you effectively sample 100 ton heaps) and finally retested the material as it was calcined.

This is certainly overkill in analysis and as far as I can remember the heaps were combined well before the analysis was available.

We had an in house machine. The attitude was that extra analysis did not add a significant cost.

Now when we had a problem with our product at a client – the client wanted results immediately.

I could understand the clients need to find out what had happened and get his furnace back on line urgently.

Downtime for a significant production unit can easily run at well over R1 million per day.

When special samples are given in the analysis they end up queuing along with all the urgent "quality samples".

With some it will be possible to get them priority – then the poor analyst has to interrupt his program to specially handle these. Even then he doesn't have time to do the special calibration requested to handle non routine samples and we get unusual samples analyzed basically by the routine method with the routine standards. The analyst rarely has time for non-routine work.

Basically the problem is that the chemical analysis section is loaded with whatever samples someone outside considers important.

Often samples are analyzed because "that looks interesting" or "if I have this analyzed daily" it will show how well I control this section.

Now that I have communicated the type of pressure the chemical analysis section is under I want to discuss the type of changes that have occurred in refractory products and the type of problems the new products pose.

When I started as a refractory technologist most refractories consisted of alumino silicates, magnesia or dolomite. The problems of analysis were to detect low levels of unwanted elements such as boron in sea water magnesia a typical mix would be:

BOF Brick

Sea Water Magnesite	100%
Organic Binder	+3%

Fire 1730°C

Ladle Brick

Andalusite	90%
Plastic Clay	10%
Organic Binder	+3.5 %

Fire 1550°C

This type of mix is no problem to analyse.

However now a typical BOF Brick would be:

Fused Magnesia		79%
Graphite Flake	1.5%	
Metal Powder		3%
Phenolic Resin		3.2%
Catalyst		0.5%

Cure 350°C

It is much more difficult to get a meaning full analysis result from this.

When this brick is heated there will be a loss in weight as the phenolic resin carbonises, then the metal powder will react with the carbon to form a compound such as aluminium or silicon carbide to protect it from oxidation. However this protection is only partial so if heated long enough in oxygen the graphite and the metal powder will oxidize. Also iron present in the magnesia and graphite will initially be reached and later oxidized.

If a sample like this is handed in for chemical analysis of a normal commercial laboratory the result obtained is quite meaningless.

The ladle bricks have also metamorphosed to be:

Iron Ladle
Alumina
Graphite
Silicon Carbide
Metals
Resin / Pitch

Steel Ladle
Alumina
Magnesia
Graphite
Metals
Pitch

Even concretes are changing from being simple mixtures of aggregate and cement to mixes of the type:

Alumina
Silica / Alumino
Cement
Graphite
Silicon Carbide
Metals
Dispensants

I would be interested to hear from any suggestions as to how I can get meaning full chemical analysis results on this type of material.

I have tended to use chemical analysis less and rely more on scanning electron microscopy which allows me to distinguish the starting phases but doesn't give a real quantitative result.

However I approach these materials there need to be more communication with the analyst to explain the material expected to be present and discuss the way it will be analyzed. Then I will know what might have been lost in the analysis and in what form I will expect any elements to have been analysis. This also needs an analyst who is less busy and has more time to devote to special requirements.