Elemental Analysis of Secondary Alumina and Phase Analysis of Alumina-Containing Materials

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Abstract

Hydro Aluminium and other primary metal producers must handle several major internal process streams of materials that are significantly changed from the original purchased raw materials. These streams include the recycled anode butts material, the anode cover material, spent potlining and, probably the largest internal material stream, the secondary alumina from the process gas treatment center. Originating as smelter grade alumina (SGA), or primary alumina, it is termed secondary alumina after use as the process gas and particulate cleaning agent in the gas treatment center.

Good analysis of these materials is part of good operational practices, and the paper describes experiences from elemental analysis of secondary alumina and phase analysis of alumina. The elemental analysis part describes developing a Certificate of Analysis, HAL_SecAl-XRF for elemental analysis by XRF. It is an 18-part set with 25 different elements based on analysis results from ICP, XRF, Sintalyzer and combustion elemental analysis. Combining several analysis methods strengthened the quality of the results, however, the set is still at in-house stage rather Reference Material (RM) stage.

The XRD phase analysis part describes some challenges experienced when selecting phases for Rietveld refinement. The purpose was to have a set that could be applied for each material received at the laboratory that contained significant SGA. SGA alumina is mostly transition forms and these must be modelled first to enable modelling of the non-alumina part of the sample. Three examples are shown including an attempt to determine the trace-level adsorbed fluoride phases collected on the secondary alumina in the GTC; a random dust sample from a smelter and a complex bag-catch with alumina in it.

Keywords: Secondary alumina characterization, XRF calibration, XRD alumina phase set.

1. Safety

Secondary alumina is an inert material at room temperature. It is a fine powder and will cause dusting. The bulk is SGA. There are adsorbed fluorides including HF(ad) and sulfur oxide, SO_3 (g) on the surface. Handling dry: Always use protective glasses and gloves when handling. Use a breathing mask if handled in a way that can cause ambient dust. Handling when wet or in water: Always use gloves – even at room temperature traces of HF(ad) will dissolve into the water. If the water is decanted and vaporized, the residue is mostly Na_2 SO_4 (s).

2. Introduction

This paper on alumina analysis has two parts. The first is on the development of HAL_SecAl-XRF which is a set of 18 reference materials for elemental analysis of secondary alumina. The second part concerns XRD work to develop a phase set for use when analyzing samples containing SGA, including secondary alumina. The work illustrates some challenges in XRD characterization of complex materials when some of the material is short range order (SRO) or amorphous, either as a major component as in secondary alumina or anode cover material, or as a minor component as in saturated electrolyte or other. The paper concerns work ongoing to improve these types of analyses.

2.1. Secondary Alumina

Hydro Aluminium and primary metal producers handle several internal process streams. The largest internal process stream is the secondary alumina which is SGA after use as the process gas and particulate cleaning agent in the gas treatment center (GTC).

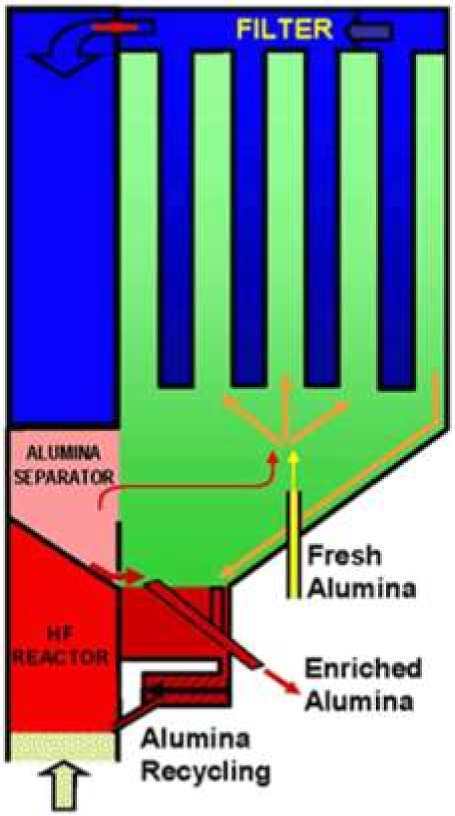

Figure 1 Gas treatment center (GTC). From GE/Alstom.

2.2. The Dry Scrubbing Process

The GTC dry-scrubber is an emission control system introduced to limit the escape of fluorides to the environment around aluminium metal plants. The GTC consists of a fluidized bed unit where the alumina absorbs pot gas emissions, and an array of filter bags to catch the reacted alumina. The collecting agent is primary alumina, Al_2O_3 , the aluminium metal raw material, and the collection efficiency for gaseous and particulate fluorides is better than 99 %. Most or all the alumina pass through the dry-scrubber bag-house on the way to production.

Primary alumina introduced into the pot gas stream works both as a free-flowing adsorbing agent to attract reactive gas and particulate in the fluidized bed part, and as a filter-cake in the filter bags to capture inert particulate. The dry-scrubber catch is released from the filter bags by pulsing every few seconds and collected in storage silos. It is called secondary alumina, reacted ore or secondary oxide.

A further development from using Short-Range Order modelling is to determine that part and subtract it from the whole diffractogram. What is left is then the more crystalline peaks and can be used for a round of phase identification.

8.2. Discussion Precision XRD

The best case is a cubic phase where the detection limit can be as low as 0.1 wt%.
For most crystalline phases, the detection limit will be 0.3 wt%.
For low-crystalline a realistic limit is 1 wt%. For Short-Range Order phases, values below 5 wt% should not be trusted as the "peak" shape then is near linear making it too close to the background. It is always better if a phase can be confirmed by visual inspection of the diffractogram.

9. Conclusions

HAL_SecAl-XRF Calibration Reference Material
An 18-sample set for calibration of elemental analysis of secondary alumina is being developed. At this stage, the quality of the set as a whole is in-house rather than Reference Material. Hydro Aluminium is interested in exchanging secondary alumina with other laboratories that do similar analysis, for comparison of analysis results.

XRD Characterization of Smelter Grade Alumina.
An alumina phase set is in use that contains alumina forms from Short Range Order phases through several modifications of increasingly crystallized alumina to the completely crystallized alpha phase. The set reliably models the alumina part in various materials from high alumina content to low alumina content. The quantification of the alumina should be controlled by addition of an internal standard. The advantage of using the set is that other, non-alumina phases can be reliably modelled.

So far, the set has not been confirmed physically or linked in a significant way to other alumina properties. That is an interesting possibility but requires considerable parallel analysis work.

10. Acknowledgement

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