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).

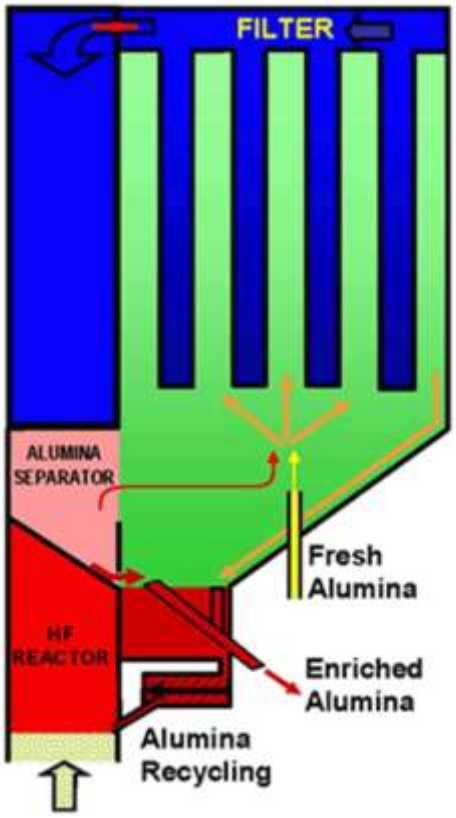

Figure 1 Gas treatment center (GTC). From GE/Alstom.

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, $Al_2 O_3$, 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.

In addition to being environmentally advantageous the economics of dry scrubbing is beneficial because the expensive fluorides are returned to production, more than balancing the cost of the dry-scrubber installation and operation.

2.3. Secondary Alumina and Impurities

Unfortunately, contaminants in the pot emission dust are collected with similar efficiency. Contaminants like C, as dust, and P, Ti, V, Fe, Ni, Cu, Zn, Ga and Pb are returned, as well as moisture and sulfur gases. The use of the dry scrubbers establishes a recirculation loop. The disappearance of one major loss-mechanism for contaminants entails an increase in others, including the transfer of contaminants to the metal. [1, 2]

The recirculation of material means that the SecAl-Bath-Emissions-ACM-Emissions loops have become repositories of Phosphorus (P) and Sulfur (S), with negative effect on the process current efficiency, energy loss, and for sulfur, greater risk of corrosive wear, and the capture and return of trace metals leads to increase in impurities in the metal.

An example for P in a metal plant gave level of P in the primary alumina as 12 ppm, while it was 300 ppm in the frozen electrolyte and about the same in the secondary alumina.

3. Calibration Set for Elemental Analysis

For better monitoring of impurities, Hydro made the HAL_SecAl-XRF set for XRF analysis elemental analysis of secondary alumina.

HAL_SecAl-XRF stands for
HAL – Hydro Aluminium
SecAl – Secondary Alumina
XRF – X-Ray Fluorescence Spectroscopy

The set started as a research project and the specific aim was to better quantify elemental impurities in the secondary alumina. An XRF application was developed by Hydro's Technology's laboratory in Årdal which specializes in x-ray-based material characterization [3]. The set is shown in Table 1; one set of standards consists of 18 different alumina samples of 50-gram each, with 16 standards of secondary alumina and 2 standards of primary alumina, to help create a wider range of concentrations for the calibration of the application.

The results in Table 1 are based on analysis results from

- SINTEF MoLab AS – ICP-MS, ICP-OES, LECO, CV-AFS and IC.
- Sintalyzer for total F, Sint-F, wet-chemical determination by ion-selective electrode using a titration instrument assembly from Methrom.
- Combustion analysis by Leco-C (CS744) and Leco-O ()
- Semi-quantitative XRF: All-element determination by Malvern Panalytical software Omnian running on an Axios MAX XRF. The dried secondary alumina was analyzed as the powder after milling and pressing to a tablet in a hydraulic press. Making glass beads was considered, but several elements occur in phases that are volatile, and there are gaseous components that are part of the adsorbed material including HF (g) and release of these might harm the Pt and other equipment.

Table 1 HAL_SecAl-XRF set consisting of 16 secondary alumina samples and two SGA's. "ICP" is a combination of ICP-MS, ICP-OES. Note the footnotes regarding Mg, Si, P, K, Cu, Hg are given below the table. C and O should be reported by Leco analysis, not XRF.

Analysis		Unit	K1	K2	K3	H1	H2	H3	H4	H5	H6	S1	S2	S3	A1	A2	A3	A4	SGA SU	SGA HO	
Leco-C	C	%	0.261	0.310	0.202	0.132	0.084	0.076	0.080	0.182	0.087	0.147	0.172	0.171	0.100	0.097	0.097	0.075	0.047	0.048	C
Leco-O	O	%	41.20	39.72	39.77	40.67	40.56	41.79	41.31	39.31	39.38	40.50	40.77	40.78	38.26	38.64	38.64	39.58	41.50	41.48	O
Sintalyzer	F	%	1.26	1.56	1.16	1.61	0.91	1.07	1.35	1.48	1.49	1.35	1.39	1.36	1.13	1.32	1.23	1.19	0.00	0.01	F
ICP	Na	ppm	6000	6300	5500	6200	4600	5400	6700	6700	6000	5800	6100	6100	4600	5100	4900	4700	3500	3500	Na
ICP	Mg[2]	ppm	9	3	3	6	2	4	4	10	5	3	3	3	2	2	2	2	0.5	0.6	Mg
ICP	Al	%	50.14	50.97	52.52	50.90	50.49	51.68	51.90	50.51	50.41	50.55	50.32	51.40	51.95	51.77	51.62	51.23	52.90	52.83	
ICP	Si[3]	ppm	110	140	120	98	100	98	52	100	54	100	100	110	62	100	62	58	50	38	Si[3]
XRF Omnian	Si[4]	ppm	110	140	120	220	155	185	185	215	185	230	200	165	225	240	235	220	170	190	Si[3]
ICP	P[5]	ppm	160	49	98	69	98	140	100	150	74	130	120	110	120	140	120	140	98	130	P
ICP	S	%	0.178	0.294	0.170	0.185	0.184	0.188	0.164	0.189	0.185	0.339	0.316	0.314	0.138	0.155	0.162	0.142	0.013	0.013	S
ICP	Cl	ppm	46	49	37	25	30	25	26	26	30	110	95	71	27	33	33	27	12	11	Cl
ICP	K[6]	ppm	59	27	24	46	14	31	53	60	58	45	51	53	45	62	62	52	28	25	K
ICP	Ca	ppm	180	230	140	160	85	110	120	200	130	140	170	180	96	100	94	93	56	62	Ca
ICP	Ti	ppm	75	67	53	58	51	46	48	50	49	48	45	47	47	48	42	44	45	45	Ti
ICP	V	ppm	19	17	14	20	11	15	15	21	17	17	14	14	16	20	15	13	8	8	V
ICP	Cr	ppm	3	1	2	1	2	2	1	2	1	2	2	2	1	2	2	2	2	2	Cr
ICP	Mn	ppm	6	0.2	0.3	0.3	4	2	1	0.5	0.3	1	0.5	0.3	0.8	0.6	0.6	0.8	0.7	0.3	Mn
ICP	Fe	ppm	1200	250	200	220	110	160	170	240	190	170	140	150	140	150	120	130	76	82	Fe
ICP	Co	ppm	3	2	2	4	2	2	2	3	2	2	2	2	2	3	2	2	0.9	0.9	Co
ICP	Ni	ppm	170	200	160	140	34	78	82	140	91	120	150	150	110	120	120	93	2	3	Ni
ICP	Cu[7]	ppm	0.3	<0.2	<0.2	<0.2	0.3	<0.2	2	<0.2	<0.2	5	<0.2	<0.2	<0.2	0.6	<0.2	<0.2	<0.2	0.4	Cu
ICP	Zn	ppm	8	0.4	3	<0.2	4	19	8	4	1	14	8	6	9	3	<0.2	10	10	5	Zn
ICP	Ga	ppm	65	67	68	70	64	67	68	68	68	68	68	64	61	65	61	63	63	65.0	Ga
ICP	Sr	ppm	2	2	2	2	0.8	4	1	2	1	3	2	3	2	2	2	2	2	1	Sr
ICP	Mo	ppm	1	1	0.8	1	0.8	1	0.9	2	0.8	0.8	0.8	0.400	0.500	0.700	0.600	0.300	<0.2	<0.2	Mo
ICP	Ba	ppm	1	1	5	1	2	1	2	2	0.9	1	0.9	1	0.8	1	0.7	0.7	0.3	1	Ba
ICP	Pb	ppm	12	10	4	11	5	9	3	4	3	9	9	9	7	10	8	8	0.7	1	Pb

Notes to the table:

[1] Mercury was below the XRF detection level, so this element was not included.

[2] The Magnesium calibration is not precise; the Mg value is only informational.

[3,4] The current Silicon calibration is based on Omnian XRF analysis because the values reported by ICP-EOS did not enable a calibration (large spread, no direction).

[5] Phosphor is not ready, possibly below detection limit.

[6] Potassium is not ready, possibly below detection limit.

[7] Copper is not ready, possibly below detection limit.

The material contains HF(ad) and the formation of volatile fluorides like $SiF_4(g)$ can occur during sample preparation for wet-chemical analysis.

ICP Analysis at SINTEF MoLab

The samples were digested in sulfuric acid, hydrochloric acid and nitric acid in closed vessels using a temperature/pressure-controlled microwave system. Totally 23 analytes were determined. Sulfur was determined by use of Leco combustion analysis and water-soluble chloride was determined using ion chromatography (IC). Parallels of some of the samples were analyzed and the results showed variation between the samples/parallels of 0 %rel to 20 %rel except for Si a variation around 30 %.

3.1. Sample Preparation for XRF

The standards are supplied coarse, not milled. It is recommended to mill the calibration materials similar to routine samples before use. The secondary alumina material needs to be homogenized and milled to proper size for XRF analysis prior to sample packing. In the SecAl XRF application standards were prepared with use of boric acid on the bottom. Each sample

was pressed 45 seconds under 27 ton pressure. Both for the calibration and in regular analysis it is recommended to press two parallels or more from each standard or sample material.

3.2. XRF Calibration and Application

The XRF application was developed according to principles established for XRF instrumentation by Malvern Panalytical. The compounds are measured in individual channels, within which settings were verified using the Check Angle and Check PHD options. The maximum time of measurement is 25 minutes per sample and was used to get an accurate calibration. However, this time could be shortened if the statistical error, CSE, was accepted to increase to 0.5 % for compounds where it is < 0.5 %.

The calibration lines were obtained by use of a linear function, and only for the aluminum and silicon calibration did the calculated calibration model include correction for effects from matrix composition (the Si calibration still failed, but due to other issues).

4. Phase Analysis of Samples Containing Smelter Grade Alumina

4.1. X-Ray Diffraction for Phase Quantification

Figure 2 is a typical XRD diffractogram of an SGA. The challenge when identifying, modelling and quantifying this material is best illustrated by comparing with Figure 3 which is a typical well crystallized material (incidental example).

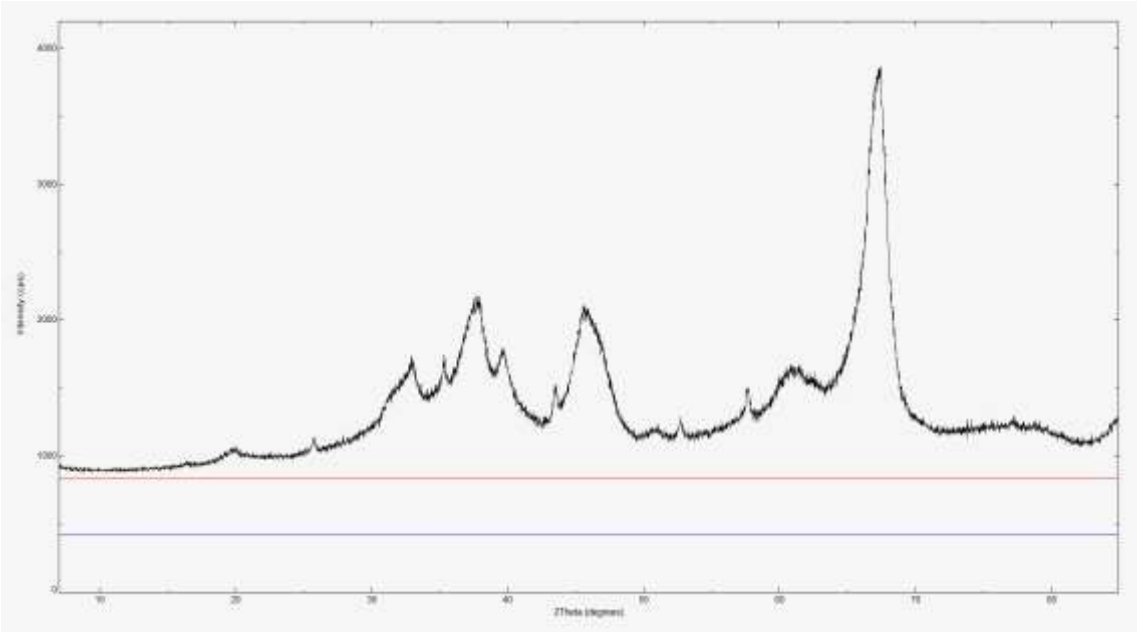

Figure 2 XRD diffractogram of a typical smelter grade alumina. Note the wide peaks; the few sharper peaks are alpha-alumina, the calcined end-product alumina.

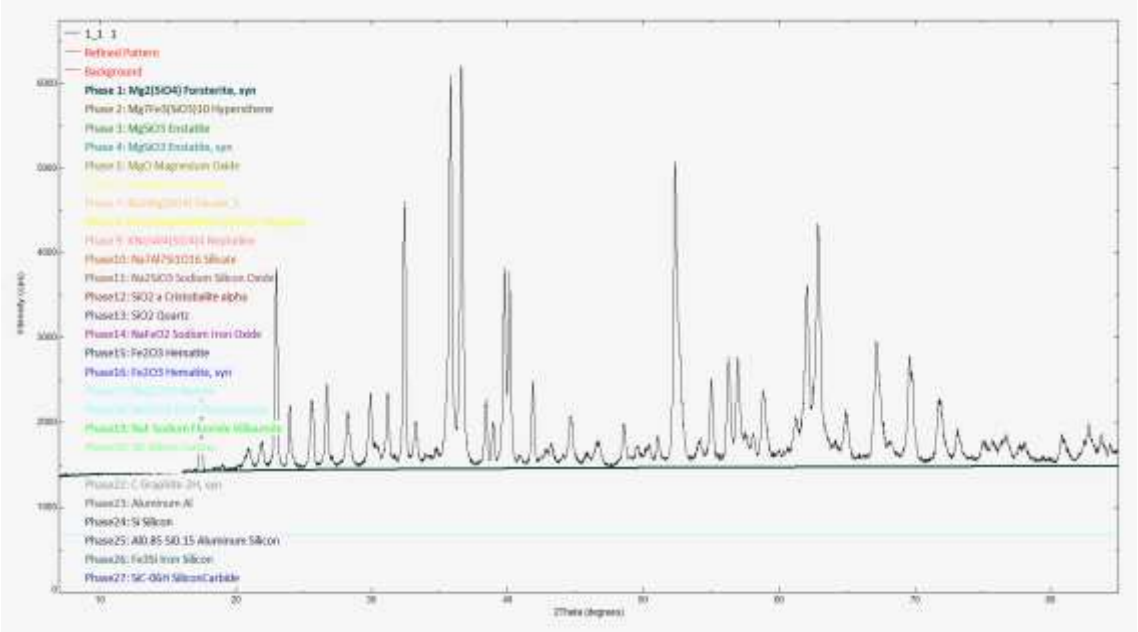

Figure 3 XRD diffractogram of a well crystallized material (incidental example shown only to illustrate the difference in peak shape from the few and wide peaks in Figure 2.

In this work the aim was to make a model of the phases present in the sample using whole profile Rietveld refinement. [4, 5] To do this successfully a good XRD scan is needed. It should minimum be over the range 10-75 °2theta with step 0.02 °2theta and counting 1 second per step. A fine focus x-ray source yields better peak resolution.

The work sequence will then be XRD scan, phase identification, phase set modelling by Rietveld refinement. This usually works with materials with diffractograms as shown in Figure 3. Three differences between that material and the SGA material in Figure 2 can be pointed out:

- For the Figure 3 diffractogram there are many, and sharp, peaks, at well-defined peak top positions; this helps the identification of the individual phases present when using a Search and Match algorithm, where peaks are compared with a reference database such as the ICDD PDF4+ or the American Mineralogical Society database. For such a peak set, the associated structures can be loaded directly from the database and used for Rietveld refinement and quantification. For the SGA in Figure 2, there are few, and wide, peaks, making a Search and Match for identification against a reference material database not practicable. So how to identify the phases composing this material, and how to establish structures for Rietveld refinement?
- In Figure 3 there are many peaks, allowing identification of multiple phases. And if this is a material often analyzed, it is possible to make a set of phases and to establish a Rietveld refinement model as an application used in routine analysis. This cannot be done without a reference set of phases, so analysis of the SGA in Figure 2 cannot follow that path for identification/quantification. Again, the question is, how to establish structures for Rietveld refinement?
- For the Figure 3 diffractogram, the background, or the diffracted intensity at the feet of the peaks, is close to linear across the scanned range. In Figure 2, a considerable part of the diffracted intensity is not obviously associated with the diffracting peaks but appears to lift the whole diffractogram up. Background in the XRD diffractogram is mostly associated with either higher concentrations of strongly fluorescing elements, or amorphous or low-crystalline material. Low crystalline material is termed Short Range Order material. For SGA Short Range Order material is the cause.

Application example: A well-known analytical task for SGA (Figure 2) is to determine the alpha-alumina content (the alpha is seen as the few narrow peaks present). However, to model and quantify the alpha by a Rietveld refinement-based method also the rest of the diffracted intensity must be modelled. This means the Short-Range Order transition aluminas making up the "background" must be modelled also.

In ISO 19500 the alpha content is determined by peak height and background height measurement and computing the difference and comparing with a 100 wt% alpha calibration; this principally simple and straight-forward method work for alumina containing materials with nearly 100 wt% alumina. [6]

4.2. Smelter Grade Alumina

Alumina from the Bayer process made through calcining of the Gibbsite precursor is a designed material, incompletely calcined, by design to make as much low-crystalline forms as possible. This makes Rietveld type phase modelling challenging.

"Transition" $Al_2 O_3$ has many possible forms as illustrated in Figure 4. The calcination paths depends both on the Bauxite precursor and the calcination technology used such as rotary kiln, fluidized bed or rapid flash technology.

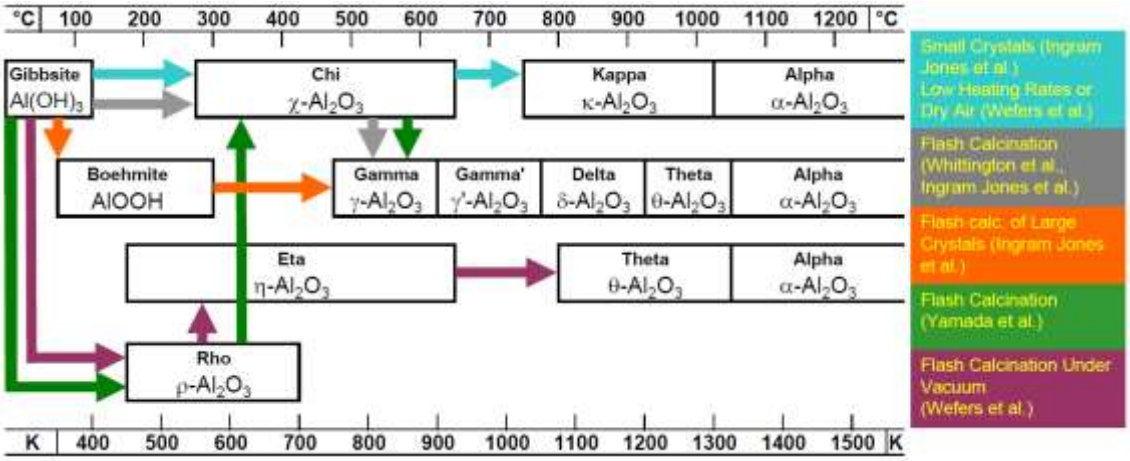

Figure 4. Calcination paths and the resulting low- to high-calcined alumina forms. Illustration from [12], Figure 3.7.

4.3. Rietveld Modelling of Smelter Grade Alumina

Since 2012 Hydro Aluminium has cooperated with David E. Simon (co-author of [4, 5]) and we have developed several phase sets of alumina forms tested as phase sets for describing SGA.

Figure 5 illustrate a moderately successful early modelling. This phase set could be used to "model away" most of the wide-peak alumina material in samples where alumina was one of the components, and this allowed stable modelling of other phases in samples. This alumina set was used both for primary and secondary alumina. A more refined set is shown in Table 2.

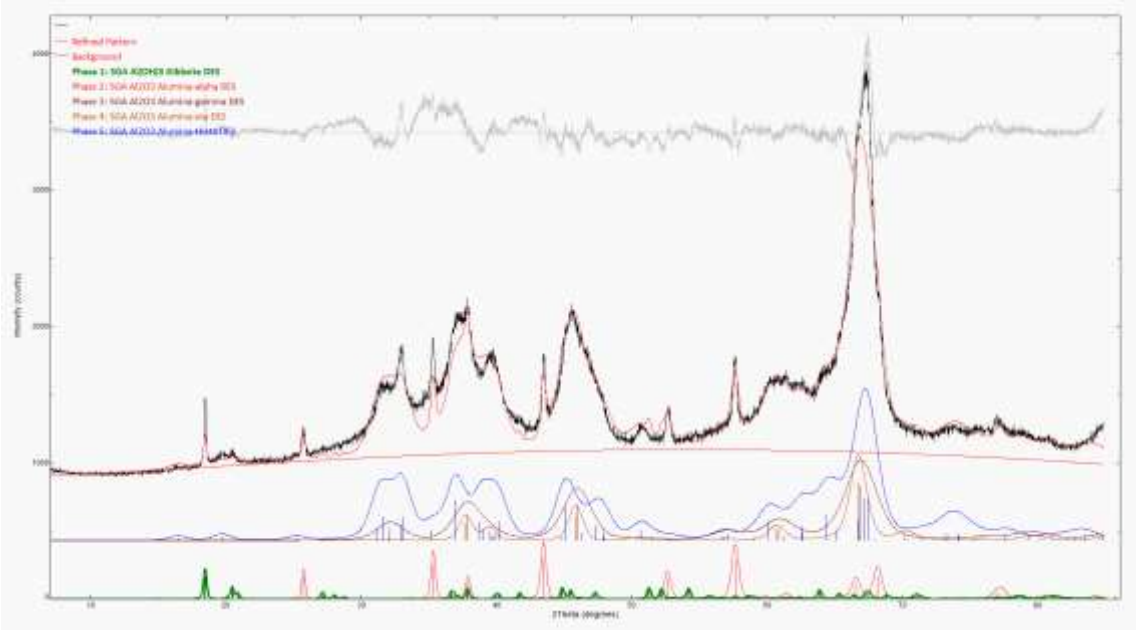

Figure 5 XRD Rietveld modelling of Smelter Grade Alumina. Early example already suited to "modelling away" most of the wide-peak contribution from the aluminas.

5. Selection of Aluminas, Al_2O_3 Forms

A considerable body of literature exists on XRD phase analysis with crystallite structures of Smelter Grade Alumina [7 - 16]. Several of these are associated with the Light Metals Research Centre (LMRC).

The crystallite structure must be available to allow Rietveld refinement. Most of the modifications of alumina shown in Table 2 were tested by selecting and adapting different phases to make a suitable set. Some were not relevant, and some were close structures which meant high correlation and breakdown in the model - then only one of the structures could be selected and used.

Table 2 Modifications of alumina with crystallite structure. Some with reference to originating authors. Yellow marker are recommended forms used in the current alumina phase set.

Alpha
Theta
Chi - unusual but seen
Delta - pre-dated gammas that seem to be the same
Eta (flash calcination)
Gamma
Gamma'
Gamma 1:1
Gamma 1:3
Kappa LRO - refined to zero
Rho (flash calcination under vacuum)
Kappa' SRO
Theta SRO
Gibbsite - $Al(OH)_3$
Boehmite - AlO(OH) - only calcination tests

6. Experiences from Modelling Aluminas

6.1. Sample Preparation

The test portion was prepared by milling down to average grain size 25 µm, then backfilling into a holder onto a filter paper; this avoids most of the preferred orientation effects e.g. from alpha platelets. Sometimes Fluorite was added as internal standard at 20.00 wt%.

6.2. Rietveld Modelling

The modelling of the low-crystalline and Short-Range Order (SRO) alumina part of the diffractogram helps stabilize the rest of the materials needing to be modelled. Especially for samples where the alumina is not the major constituent, care must be taken when adding the non-alumina phases. When loading a phase from the ICDD PDF4+ or similar, refinement should initially be limited to the scale factor, and the scale factor should be adjusted manually to a near-correct value.

- For quicker convergence, the Unit Cell should be fixed till peak shape is stabilized – unit cell parameters a, b, c, α, β, γ.
- For the scale, if the start value is overestimated, other phases can be "washed away" so start conservative which means low.
- One means for increasing confidence in the alumina result is adding e.g. CaF_2 Fluorite internal standard at 20.0 wt%.
- For the first run, the peak shape U and W parameters (Cagliotti model, Table 3) should be set, not to the instrument values but to an estimate for U and W taken from another phase with similar peak shape.
- For minor phases it can help to keep U or W fixed and release in a later round. This can help retain minor phases that otherwise could disappear early due to variation during the large phase fitting.

Table 3 Cagliotti peak width parameters U, V, W. Note that V must be set to the instrument value and not refined.

$H^2 = U * \tan(\theta)^2 + V * \tan(\theta) + W$			
U, W examples	Alumina Form	U	W
	Alpha	0.15	0.04
	Gamma	0.7	0.7
	SRO	20	20

When the low-crystalline and Short-Range Order alumina part in the material has been stabilized in this way it is possible to test factors that make the shape of the peaks and the intensities deviate from regular crystallites such as Preferred Orientation effects in the material, or strain and crystallite size effects.

Using this method, a moderately good refinement fit was achieved with a transition alumina set that appeared to be sufficiently well defined to model the alumina contribution and to allow some quantification of the fluorides.

6.3. Example: Material with Alumina as Major Constituent

Several types of materials from the metal plant can be analyzed such as general dust from floors, bath/alumina from the basement or bath/alumina from the Gas Treatment Center. The diffractogram of one such sample is shown Figure 6. Here the alumina part is 85 wt%, with more than 30 wt% as Short-Range Order alumina. The non-alumina part was electrolyte bath components including Na_3AlF_6, $Na_5Al_3F_{14}$, $NaAlF_4$, alpha-$NaCaAlF_6$, alpha-$Na_2Ca_3Al_2F_{14}$ and carbon. The model alumina set allowed speciation and quantification of the non-alumina material.

It should be mentioned that this analysis was not complete; note the peaks in the bottom grey trace which is the non-modelled intensity; it is overall linear but with several obvious peaks.

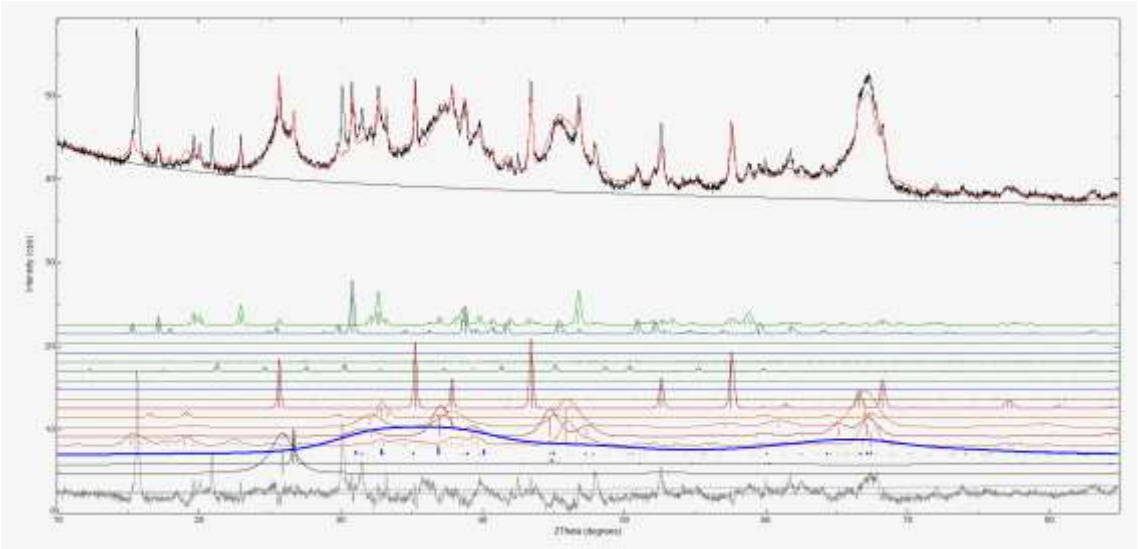

Figure 6 XRD Rietveld modelling of a high alumina dust sample. The difference between recorded intensity and model is the grey trace lowest in the chart. The blue line illustrates a Short-Range Order alumina. Diffractogram recorded on a Bruker D8 instrument at the Norwegian University of Science and Technology in Trondheim, Norway.

6.4. Example: Material with Alumina as Minor Constituent

Material from butts cleaning with 50 wt% carbon and 17 wt% alumina. The example illustrates that a similar technique to the method used to model Short Range Order alumina can used for Short-Range Order turbostratic carbon. This carbon component is typically from petroleum coke and anodes. This modelling of carbons is especially useful with samples of dust or otherwise high in carbons from the anode plant.

6.5. Example: XRD Modelling Regular Secondary Alumina

The aim was to use the alumina phase set with electrolyte bath components to see if the fluorides could be quantified. The alumina part dominates the SecAl and the fluorides are a very minor part < 1 wt%. However, it was not possible to either identify or quantify the non-alumina crystalline phases.

7. Discussion

A similar technique to the method shown here for alumina can used for Short-Range Order silicates that can occur in Spent Potlining, or for any high-carbon dust with a Short-Range Order turbostratic carbon component from petroleum coke and anodes. The modelling of carbons can be useful with samples of dust as in Figure 7.

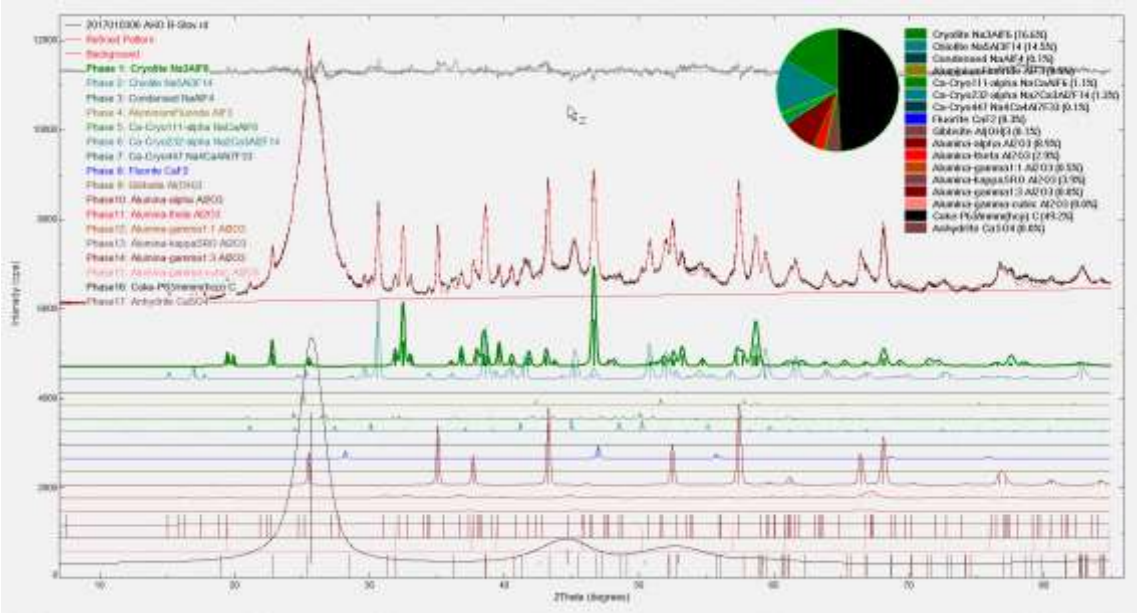

Figure 7 XRD Rietveld modelling of a low alumina and high carbon dust sample. The difference between recorded intensity and model is the grey trace at the top of the chart. Diffractogram recorded on a CubiX Pro instrument at the Hydro Aluminium Technology x-ray laboratory in Årdal, Norway.

7.1. Example: XRD Modelling Regular Secondary Alumina

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A similar technique to the method shown here for alumina can used for Short-Range Order silicates that can occur in Spent Potlining, or for any high-carbon dust with a Short-Range Order turbostratic carbon component from petroleum coke and anodes. The modelling of carbons can be useful with samples of dust as in Figure 7.

8.1. Further Improvement

In our current system, the phase composition from XRD is converted to an elemental composition and compared with XRF and Leco-C, -N, -O elemental values. The comparison usually is good, however, the comparison can be used as a feedback loop to adjust phase modelling parameters toward better value reporting.

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.

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