Analysis of Materials for Production and From Production

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Abstract

The metal plant will have major and minor process streams of materials. Materials purchased for the production are well characterized, with a certificate from the supplier, and there will be an onsite laboratory for critical quality checks - and underneath all this is an extensive support structure and knowledge base including instrument suppliers, ISO standards and suppliers of Reference Materials.

But for some minor process streams, some recurring waste, and incidental unknown materials this support structure might be not-so-helpful, or maybe non-existing. Hydro Aluminium has addressed this issue. Starting with experience from our onsite analysis of materials for production, principally quality control, Hydro Aluminium has established a practical approach to what we call Complex Analysis. Some of the methodology will be described and examples will be given that include random dust, new and used refractory, new and used cell materials, and electrolyte bath mixed in with other material in several forms.

Complex Analysis uses smart sampling, imagery and XRD phase analysis supported with XRF to understand the material. The XRF matrix modelling is supported with combustion analysis, electrochemical titration and XRD to include the light elements. Risk evaluation and HSE concerns are addressed in all these steps.

Hydro Aluminium has established an effective operational procedure for handling a wide and increasing range of materials from production. And an added benefit is that when materials begin to be well characterized, they can be established as internal Reference Materials, and used when building calibrations.

Keywords: Aluminium reduction technology, Material characterization, X-ray analysis, Spent production materials, Waste to value.

1. Introduction

1.1 Safety

Safety precautions must be respected such as wearing gloves, eye protection, breathing mask and handling in a ducted fume hood when required.

This type of analysis work will see many and different types of samples; there will be fine powders and there will be dusting. Some will have fluorides or adsorbed gases including HF(ad) and sulfur oxide SO_3(g) on the surface.

1.2 Key Analysis Methods

The characterization of materials is much enhanced by XRD phase analysis, especially when using Rietveld modelling for quantitative determination. The methodology has evolved around this, and the flowchart illustrate steps that usually give a good analysis. As a first step, it is helpful to have the approximate XRF composition, the raw data, to enable early start of the XRD phase determination. It is normally known where the material is from, and a probable composition, and an XRD scan will confirm and clarify further.

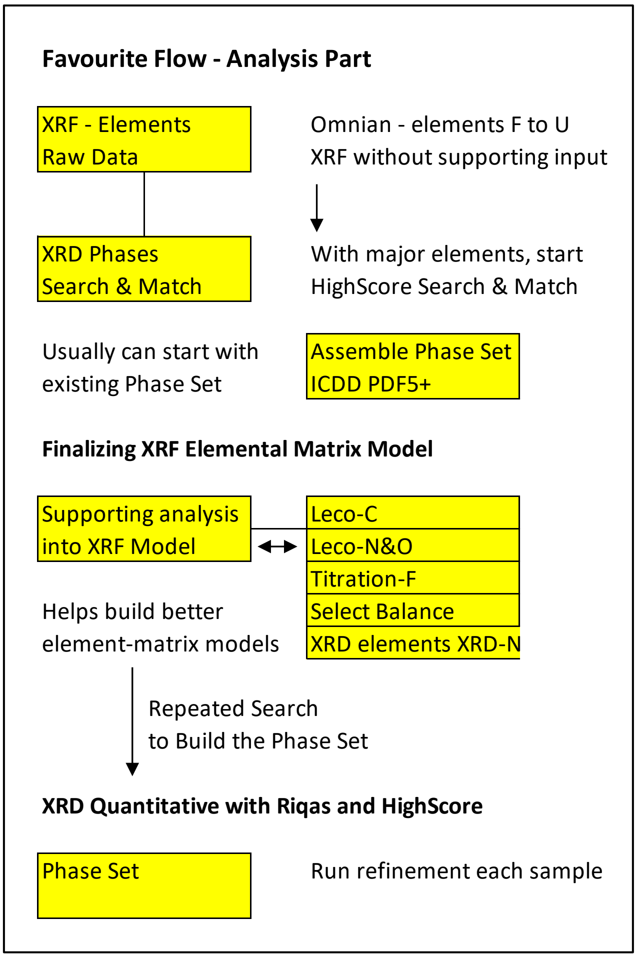


Figure 1. Flowsheet: The yellow boxes are the steps and the text next to it gives relevant information. "Favourite Flow" is the learning step, in "Finalizing XRF" the important XRF model is developed and the work finishes with the XRD model.

Sometimes a good starting XRD Phase Set might already exist, and just some small Search & Match based on the XRF elements will be used to enhance the Set.

The supporting analyses are a powerful tool when integrated into the XRF model. C, N, O or F, and more, can be added as a Known into the matrix model, at the known, fixed value.

Another powerful tool is to set one of the major components as "Balance". E.g. for spent lining, C-Balance is logical as C is major, and is not quantified by the XRF analysis itself. But as Balance, C is actively integrated in the element matrix.

The most interesting part, analytically, is the rounds of Search & Match for possible XRD phases. This generates the understanding of the material, and is achieved through literature, or using HighScore with the ICDD PDF5+ database or consulting with external expertise.

1.3 Material Types in Analysis

XRD Phase Sets have been developed for many materials present at the metal plants. Some less complex materials, or materials that might seems so due to being so common, are

- Electrolyte bath
- Anode cover material (ACM)
- Cell process gas and deposits from the Gas Treatment Center (GTC)
- Secondary alumina
- Spent potlining (SPL) including SiC-sidewall and the graphite cathode-blocks

Some recurring more complex materials are

- Materials from cleaning systems including refractory filters and dust/residues
- Foundry slags, mapping lining conversion
- Spent cell linings and spent baking furnace refractory
- Anode service, slags, or mapping the conversion of refractory in iron furnace
- Incidental dust, and incidental lumps – sometimes very special, but often it is bath or ACM made unrecognizable by carbon dust – a little C-dust goes a long way.

2. Example 1, Working with Anode Cover Material, ACM

The complex diffractogram below is of a low-transition alumina ACM which is typical for old and not-so-good ACM. The complexity of peaks indicates there is much potential information, and experience has confirmed this.

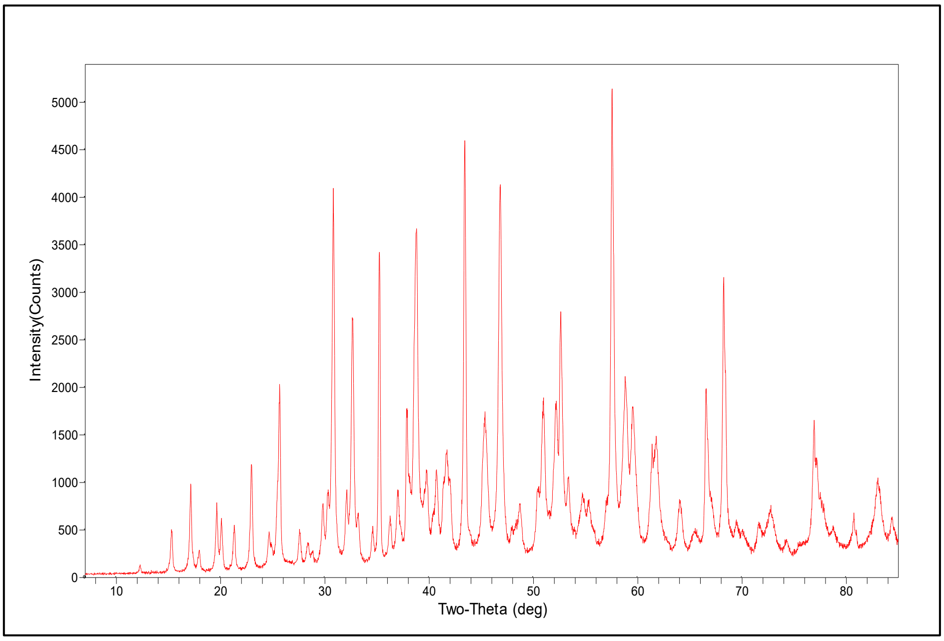


Figure 2. XRD diffractogram of Anode Cover Material (low transition-Al_2O_5 alumina).

2.1 Using a Phase Set

ACM is a mix of frozen electrolyte and secondary alumina, with some carbon/graphite build-up in recycled material over time. More phases are added into the set at need. Maximum allowable is 30 phases. Hydro has worked with the phase analysis of ACM sufficient to be able establish a simplified routine phase determination that allow hundreds off samples to be analysed yearly. This is an example of how the Complex Analysis method can yield a practical solution to analysis. Such a benefit is possible when a recurring material begins to be well characterized.

ACM is a mix of frozen electrolyte and secondary alumina, with some carbon/graphite build-up in the material over time.

In practice all the systems of bath, ACM, pot gas and secondary are well described with

- 9 bath fluorides
- 9 alumina phases
- 3 carbon/graphite phases

and Al-metal (just to be sure)

More phases are added in at need.

2.2 The Phase Set Concept in XRD

The Phase Set or Phase Filter concept is based on work by Robert Morton and David E. Simon [1]:

A rapid multiphase Rietveld X-ray diffraction analysis combined with a non-destructive multi-element X-ray fluorescence profile of samples leads an x-ray lab towards descriptive material science.

A “Phase Filter” is an assembly of phases that possibly could be present in materials of interest and that repeatedly is used for analysis of these materials. Having the Phase Filter ready simplifies traditional Rietveld modelling, with corresponding decrease in time per sample.

The usefulness is partly due to the reliability of the Rietveld full-profile XRD modelling. The model calculates every data point in the diffraction pattern, including background and all contributions from the phases, and scales the content of this model to the actual X-ray diffraction data of the material.

The Complex Analysis as used by Hydro is a practical approach for developing and using Rietveld Phase Sets.

3. Example 2, Unknown Collected in Proximity of Electrolysis Cell

When collected it appeared similar to a geological stalagmite, upstanding with a wider base; the photo shows the pieces. Color was blackish and surface appearance was smooth/shiny.

The sample was found in proximity of an electrolysis cell and the hypothesis was something dripping off something and freezing quickly, causing the upstanding stalagmite-like formation.

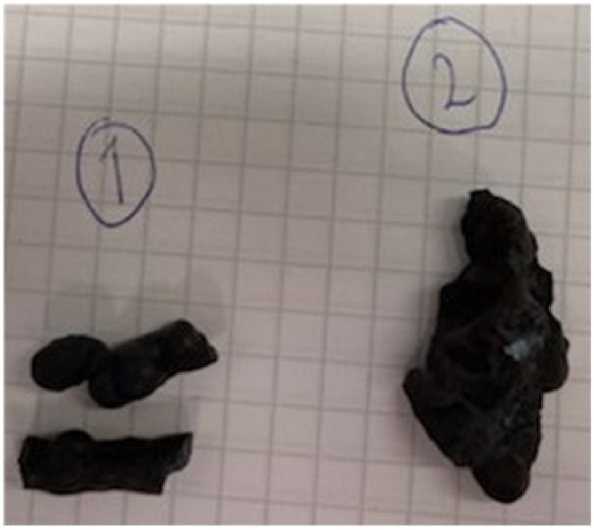


Figure 3. Pieces of stalagmite-like sample.

- Hypothesis 1: Bath
- Hypothesis 2: C-rich ACM
- Hypothesis 3: Al-metal
- Hypothesis 4: Iron, steel
- NOTE: Source is Hydro Aluminium Metal Internal Reference 2022020809, Stalagmite-Like Unknown, Jørn Rutlin and Lorentz Petter Lossius, 2022.

Some of the XRF results are shown in Figure 4, pointing toward iron as major. At this stage we – maybe a bit late – checked for magnetism, which was quite strong.

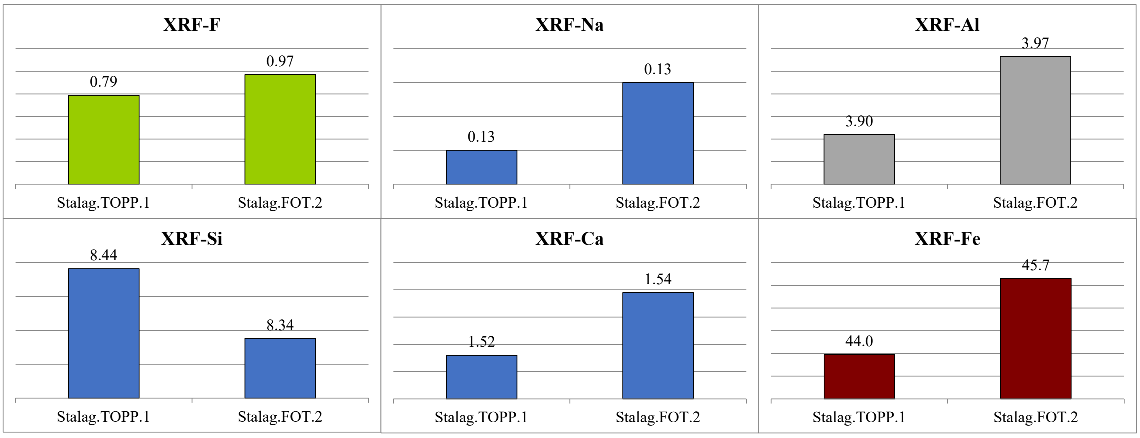


Figure 4. Stalagmite-like sample – the major elements are F, Na, Al, Si, Ca, Fe. With Fe > 40 % as the element, the oxide will be > 70 % so this was the major part.

The diffractogram, Figure 5, shows that the refined model (red) agrees quite well with the diffractogram (black). A blow-up pai-chart shows fayalite and wustite (magnetic) as major phases. We would say this also pointed toward Hypothesis 4, and we landed on this interpretation:

Steel has melted and dripped down to form the stalagmite which has corroded/oxidized in-situ. Somehow Si has gotten into the Fe-melt (no obvious connection Si-source, maybe SiC dissolved into Fe-melt).

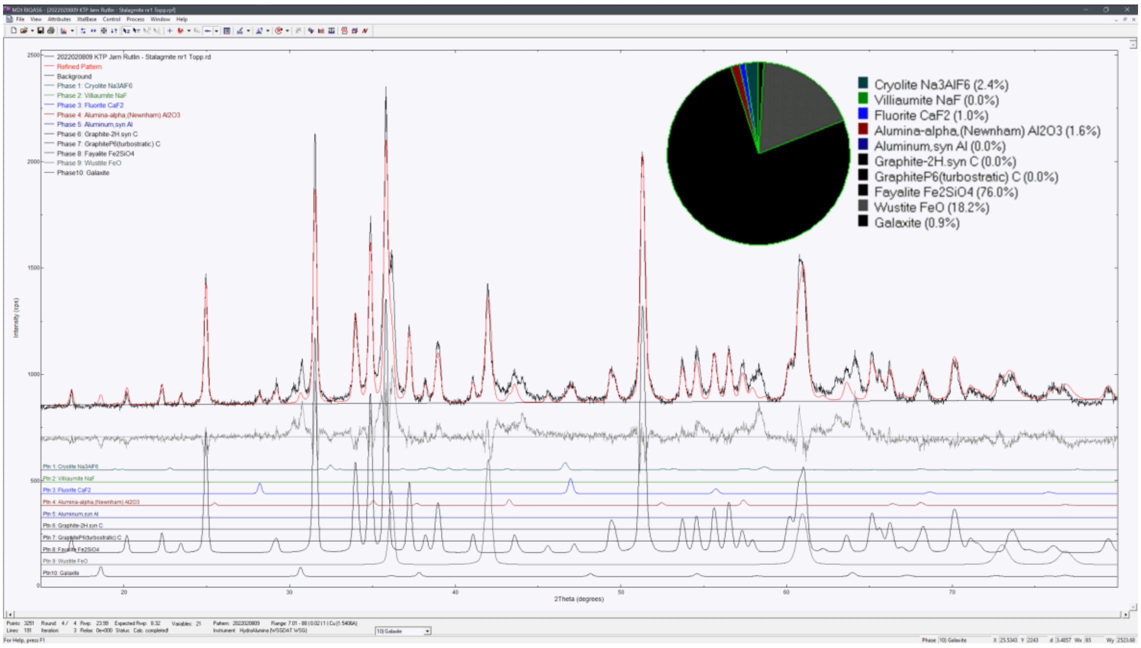


Figure 5. Stalagmite-like sample – full XRD analysis.

4. Example 3 - Spent SiC Sidewall

This example is presented as a set of six panels. They are meant to be shown each full screen in the presentation, to better show the phases. This is a relatively complex material, both as the fresh block and the spent block. The series of panes illustrate how different material properties can be looked at in one diffraction scan. Focus was on exposure damage in the spent material.

- Pane 1, upper left, just the raw XRD diffractogram scan
- Pane 2, upper right, the phases that describe the original Silicon Nitride-bonded Silicon Carbide sidewall block material, Phase 1-6 SiC/Moissanite (grey) and Phase 7-10, Si-N-O binder (blue).
- Pane 3, middle left, two phases that might represent left-over material from the production of the SiC aggregate, Phase 11, unconverted Si-metal and Phase 12, unconverted graphite (both black).
- Pane 4, middle right, Phase 13-15 (red), these are the exposure damage phases, specifically the Sodium Catena-silicate Na_2SiO_3 which is found in "soft" spots on the SiC block.
- Pane 5, low left, Phase 16-18 from the electrolyte bath (green) and Phase 19-20 (brown) which are alpha-alumina (Corundum) and beta-alumina (Diaoyudaoite).
- Pane 6, low right, adds Quesongite, the W-carbide (blue line) from the mill (SiC is abrasive) and finally some quite minor "may-be" phases, two carbonates and magnetite.
- NOTE: The source is Hydro Aluminium Metal Internal Reference 2020060806 (ASU B024), Collecting SiC Sidewall Materials from the Metal Plants, Karin Bolstad, Lorentz Petter Lossius, 2020

As seen, several aspects of material in study can be reviewed through the Complex Analysis method, in this case mostly the XRD phase part.

A comment on "may-be" phases. Such "may-be" phases are normal to a Phase Set as there will be possibles, and by including these perhaps the next batch of similar material will confirm that the phase is present, or not.

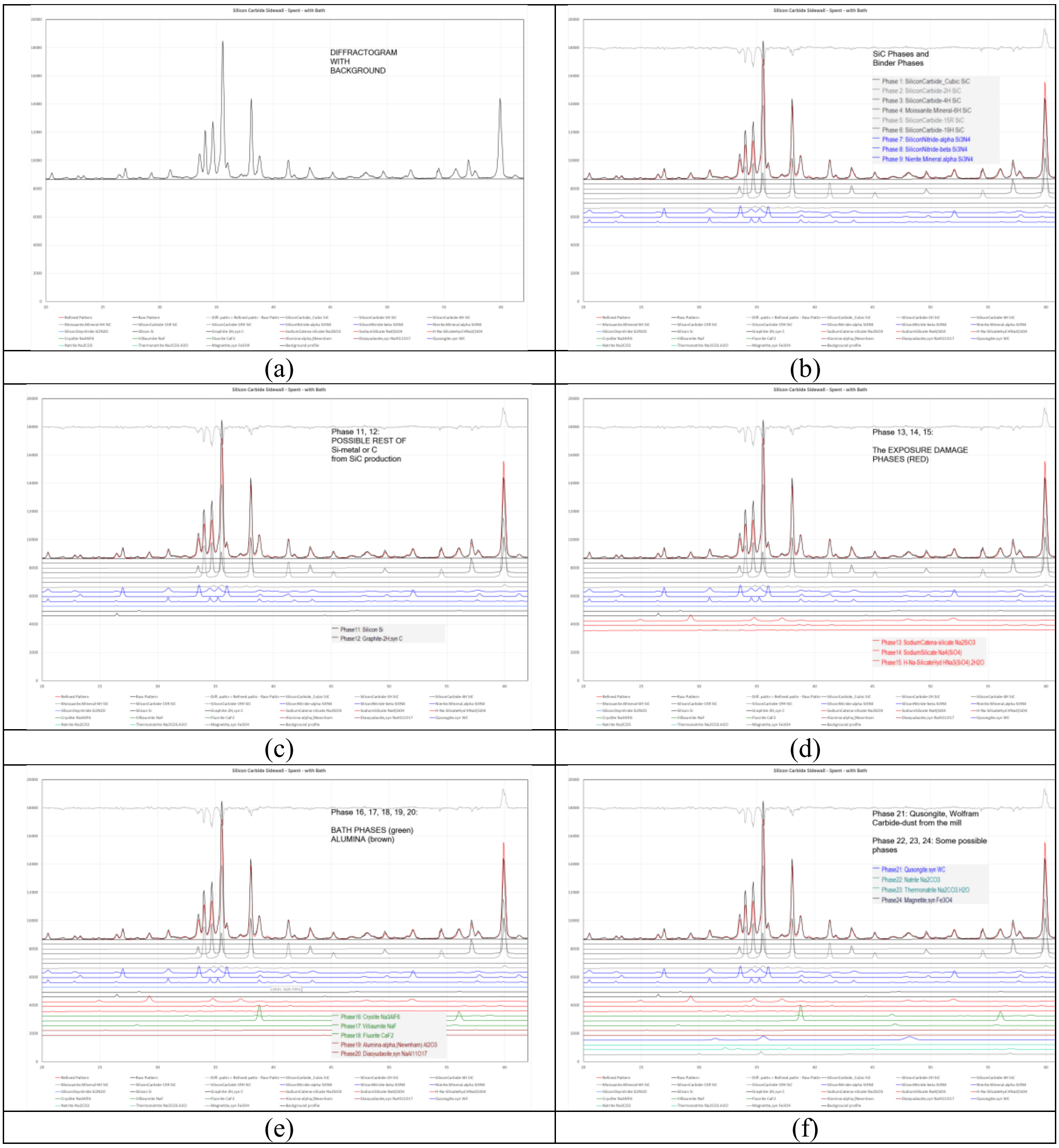


Figure 6. (a) is raw scan, (b) is the material phases of fresh SiC (grey) and Si_3N_4-binder (blue), (c) adds Si-metal and carbon which are possible left-overs from the SiC production, (d) is the exposure damage phases (red). (e) is bath and alumina (green and brown). (f) adds quesongite, W-carbide (blue line) from the mill (SiC is abrasive) and finally some quite minor "may-be" phases, two carbonates and magnetite.

5. Example 4 – Honeycomb with Non-Crystalline Part

Honeycomb is a refractory material used in the baking furnace RTO (Regenerative Thermal Oxidizer) gas cleaning system. The issue to investigate was: Too much dust in the ducting.
The parts of the Complex Analysis are seen in table 1 below with

- Photo from the sample preparation
- Titration-F and Leco-C as supporting analysis
- Some XRF elements model results (as oxides) and some XRD model results

- NOTE: Source is Hydro Aluminium Metal Internal Reference 2024042401 Honeycomb RTO Baking Furnace Condition NEW, USED, DUST, Inge Holden, Robin Stokke, Lorentz Petter Lossius, 2024.

Table 1. Honeycomb refractory – Key parts in the complex analysis.

Sampling - Photo USED Honeycomb	Supporting Analysis NEW and USED
	**SUPPORTING ANALYSIS** NEW USED Fluor % 0.003 0.003 Leco-C % 0.047 0.044 **XRF OMNIAN MODEL** MODEL AS OXIDES KNOWN C, F BALANCE Al_2O_3 **XRD** Internal Std 20.0 % CaF_2

XRF Elements, segment NEW and USED

[wt%]	NEW	USED
Leco-C	0.047	0.044
Titr-F	0.0030	0.0030
XRF-Na2O	0.32	0.39
XRF-MgO	3.5	6.0
XRF-Al2O3	62.4	44.0
XRF-SiO2	27.6	40.8
XRF-P2O5	0.098	0.157
XRF-SO3	0.0050	0.0280
XRF-Cl	0.0050	0.0060
XRF-K2O	0.97	0.74
XRF-CaO	0.29	1.19
	Etc. to U	

XRD Phases NEW and USED

XRD Phases	NEW	USED
01 Alumina-alpha,(Newnham) Al2O3	10.6	43.4
02 Alumina-theta,(Zhou) Al2O3		
03 Alumina-gamma,(Zhou) Al2O3		
04 Alumina-theta-SRO,(Zhou) Al2O3	12.0	6.1
05 Quartz-low.(Sair) SiO2	1.4	0.5
06 Cristobalite-alpha SiO2	1.2	0.3
07 Cristobalite-a.distorted SiO2	0.6	
08 Cristobalite-beta SiO2	0.1	
09 AmorphousSilica.(Sair) SiO2	12.8	9.3
10 Tridymite SiO2		
11 Mullite(3-2).(Sair) Al6Si2O13	20.0	19.7
	Etc.	

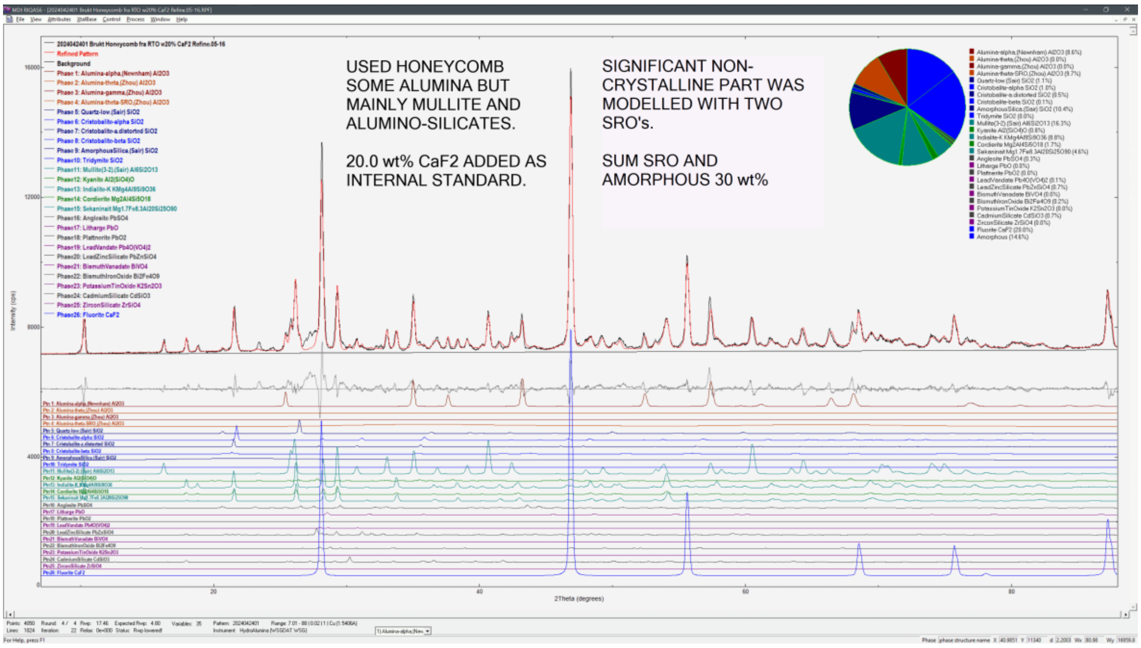
5.1 On Including Amorphous Material in XRD

The Rietveld full profile quantitative analysis was based on a Phase Set with 28 phases, plus Fluorite which was added in as Internal Standard at 20.0 wt %.

The less crystalline part of USED Honeycomb was modelled close to 30 wt % amorphous with:

- Theta-Al_2O_3 (SRO, Short Range Order, Phase04, 6 wt %)
- Amorphous silica (Phase09, 9 wt %)
- Plus, the internal standard indicated another 15 wt % amorphous giving.

The NEW Honeycomb had 7 % amorphous from the Internal standard giving a sum of SRO and amorphous of 12 + 13 + 7 or 32 %, close to USED Honeycomb percentage. From this we could conclude the dust was not poorly sintered refractory.



USED HONEYCOMB SOME ALUMINA BUT MAINLY MULLITE AND ALUMINO-SILICATES.

20.0 wt% CaF2 ADDED AS INTERNAL STANDARD.

SIGNIFICANT NON-CRYSTALLINE PART WAS MODELLED WITH TWO SRO's.

SUM SRO AND AMORPHOUS 30 wt%

Figure 7. XRD diffractogram of USED Honeycomb.

6. Discussion – Running Analysis and Upkeep of The Instruments

Laboratory safety was mentioned in the Introduction and is important throughout.
A second point through the work is Instrument Use and Maintenance which is discussed here.

Points to keep in mind when running analysis on a range of samples of widely differing composition is how to ensure the instruments can handle the materials, and how to ensure stability in the results. Some materials are very aggressive, like hydrated sulfates, or fine metallic powders. And much of X-Ray analysis is about preparing powder samples. Here are some experiences with the relevant instruments.

Combustion Analysis for total content of C, N, O, S. This has precision of two to three significant digits and the detection limit (LLD) is usually better than 0.001 %.

- Leco TC 600 for Nitrogen and Oxygen
- Leco CS 744 for Carbon and Sulfur.

The Hydro Technology Lab has strong procedures for fluoride-sensitive instruments like Leco. This is necessary for instrument survival. With Leco-O, which is a dry non-aqueous combustion analysis, quite aggressive volatiles can evolve. This is an instrument that was developed for finding oxygen in steel, at our laboratory the instrument instead is exposed to fluoridic and sulferous volatiles. The laboratory is solving this by an accelerated maintenance plan including switching the instrument innards twice during the instrument lifespan, also changing filters more often, one filter for each 15 analysis and cleaning with steel wool to remove residue just over the crucible. And we would recommend generally adding more carbon powder to the sample to ensure complete combustion.

Leco-C – many different types of samples are also run on the Leco-C, e.g. secondary alumina, which with surface HF, H_2O and SO_2 represent a similar challenge to instrument upkeep.

Fluoride Determination using a Methrom unit for the total F content by aqueous titration with F-ion selective electrode. Precision two to three significant digits. Detection limit (LLD) better than 0.001 %.

For the Fluoride titration, complete dissolution of samples is of course critical, and in the solution, to use the more active phosphorous acid as buffer and not a commercial variant. This is based on the Aarhaug paper [2] and experience at our laboratory confirms this, giving reliable results for a variety of F-containing samples.

XRF Analysis for Elemental Composition We are using a Malvern Panalytical Axios x-ray fluorescence spectrometer with SuperQ control software. For most calibrated applications we see precision two to three digits and LLD 2 ppm for elements above K; 5 to 20 ppm down to F.

In this Complex Analysis work the main application is **Omnian for elements** – a general software for elemental matrix modelling using Fundamental Parameters. Precision two digits and LLD 0.001 wt % for Ca and higher and material dependent down to F. A strong point to this application is that light elements including Li and C can be added into the matrix as Knowns, significantly improving the matrix model.

XRD Analysis for Phase Composition: We are using a Malvern Panalytical CubiX Pro diffractometer with X'Pert control software and with HighScore Plus Ver. 5.2 XRD analysis software. A second analysis software is Materials Data Inc. Riqas 6.5.1 (this has a simpler user interface than some XR-software – but unfortunately, Riqas development was discontinued in 2018).
Riqas was supplied with the AMCSD (American Mineral Society) database. Out main database is the annual subscription ICDD PDF5+. Re precision, we generally find XRD has precision one to two digits and LLD for phases with distinct peaks 0.2 wt %, but quite material dependent.

7. Improvements

For Hydro Technology Lab, our XRD analysis has long relied on a CubiX with a single point detector. We now have access to a CubiX XRD with array detector, and the difference in counts is illustrated. See Figure 8, the upper pane has both scans against the same y-axis, illustrating the difference in counts, and the lower pane has old scan (orange, "POINT") on the Y2 axis.

8. Conclusions

Based on experience, we recommend "Patient XRD – there is always one more sample coming". Developing a good phase set takes more than one sample; major phases are easy, but the medium and minor will require some development time. Maybe in the next sample a minor phase with only one peak showing might present you with a bonus three peaks!

In early phase set development there will be lots of maybe. When you are collecting samples for such work, consider that a series of related samples is good, and variation is good.

Next, as shown here, good supporting analysis makes a great difference. Over time, the list of usefulness might be sorted as Leco-O, then Titration-F and Leco-C. It is only more recently we have realized that good XRD also can supply support for the XRF matrix model from elements determined by phase stoichiometry; we now, e.g., look for XRD-N rather than Leco-N to use in modelling the element matrix.

Lastly, and fundamental to the work is the preparations of the samples. We assume that operations have sent what they mean us to characterize. But starting from that, always ensure you are documenting well with photos, and a log of actions and results. In our system we can go back more than 5 years, to compare with a current material and handling, this is very helpful.

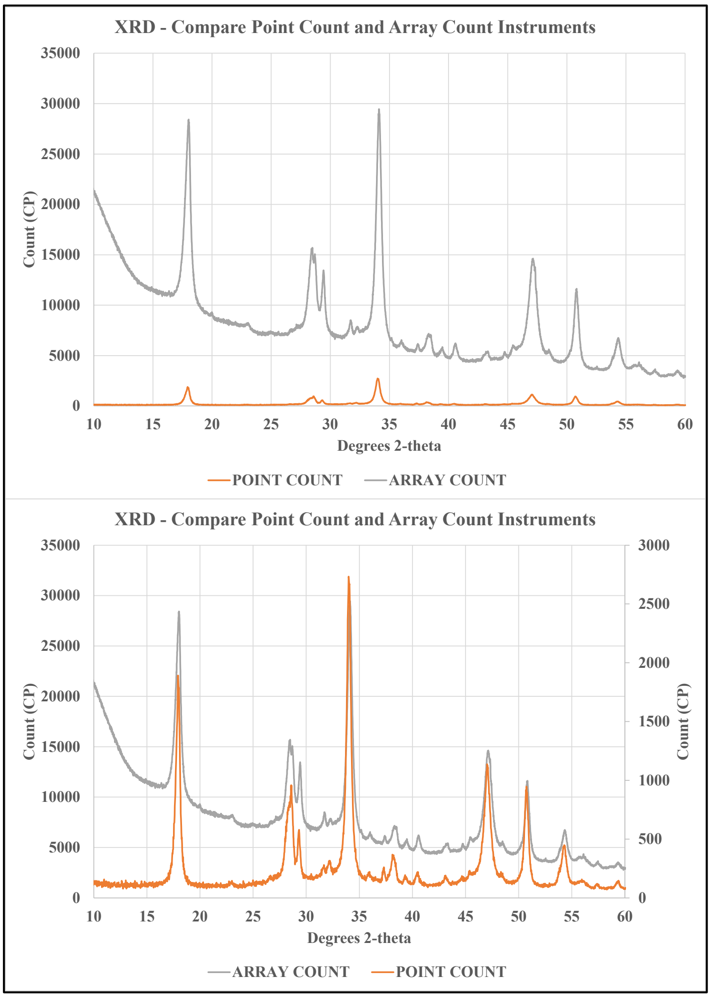


Figure 8. Improvement XRD - better counting statistics with better array detector. In lower pane old scan is on right Y2 axis, illustrating count difference.

9. Acknowledgements

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10. References

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2. Thor Anders Aarhaug, Kalman Nagy, Kieran G Smith, Potentiometric Fluoride Analysis with Improved Analytical Performance, *Light Metals.* 2012, 769–772. 10.1002/9781118359259.ch132.