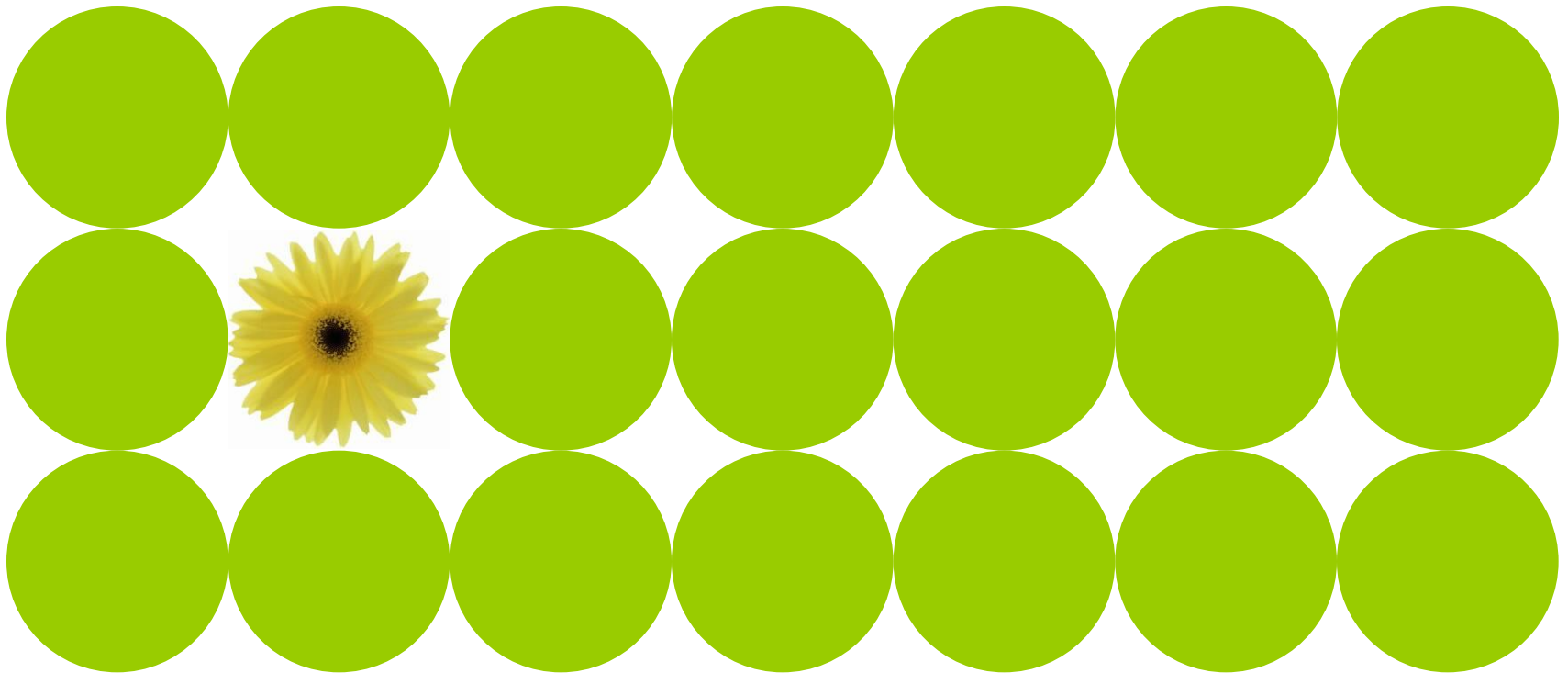


Test Portion Grinding Fineness and XRD Diffractogram Quality in Rietveld Phase Quantification



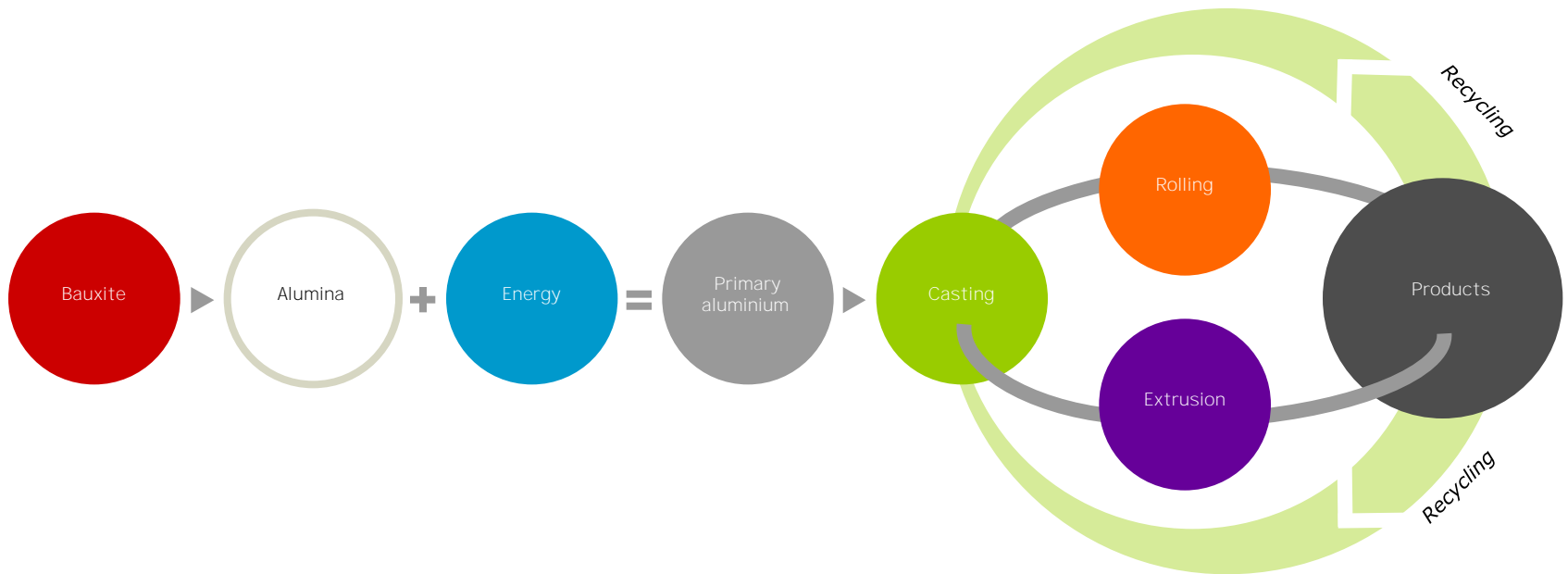
Lorentz Petter Lossius, Hydro Primary Metal Technology, Årdal, Norway

E-mail: Lorentz.Petter.Lossius@Hydro.com

Hydro Aluminium

- Based in Norway with operations in 40 countries
- 23 000 employees
- 3.8 million metric tons (primary, remelt, recycling, cold metal)
- Operating revenues 2011: 91.444 NOK million

Value chain - Fully integrated



Upstream production facilities



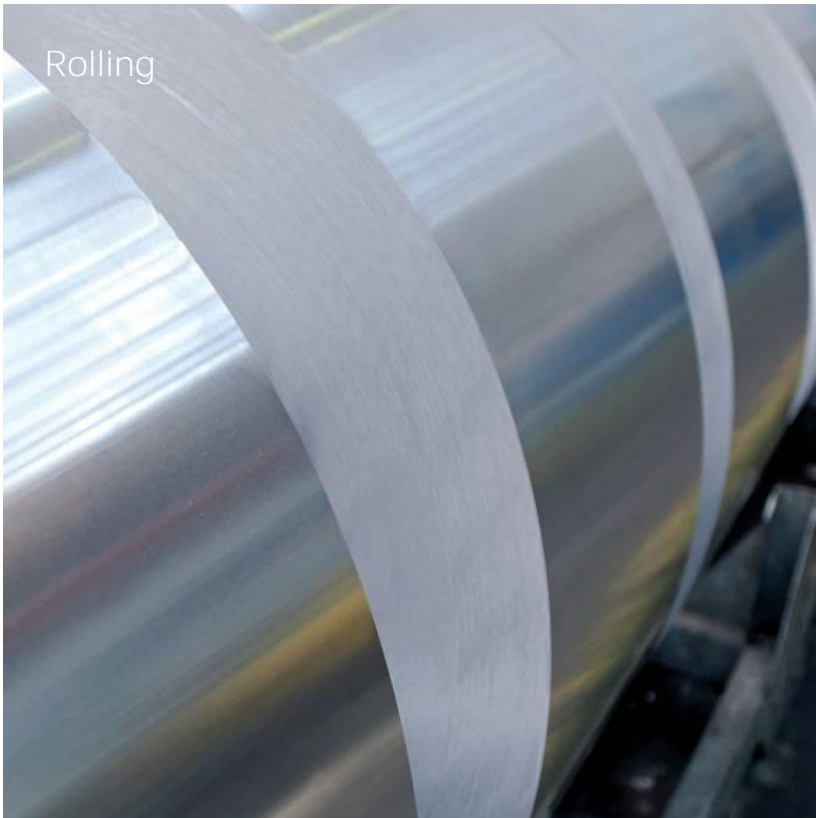
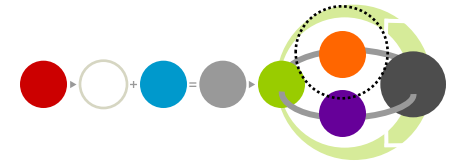
- Bauxite/alumina
- Smelters
- Remelters

Aluminium downstream worldwide network



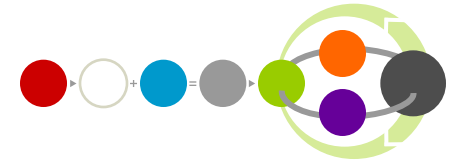
- Extruded Products
- Rolled Products

Rolled Products



- 1 million metric tons per year
- Regional business
- Close to customers
- Innovation
- Market leading in litho and foil

No. 1 flat rolled products producer in Europe



Packaging
& building

Revenues:
NOK 11.3 billion



- World leading position
- Record results
- Technology leadership and innovation

Automotive, heat
exchangers
and general
engineering

Revenues:
NOK 6.8 billion



Litho

Revenues:
NOK 3.7 billion



Test Portion Grinding Fineness and XRD Diffractogram Quality in Rietveld Phase Quantification

Aluminium smelter operation needs analysis of process streams for monitoring the stability of chemical properties. X-ray diffraction is used both for routine monitoring, and for research purposes on these materials. Some of the materials such as smelter grade alumina and anode cover material are complex with components of very different hardness. The presentation gives example of quantitative analysis with focus on grinding and grain size distribution. Tests have been run with different samples (bath electrolyte, anode cover material, smelter grade alumina) on several grinders (swing mill, mortar, McCrone Micronizer) to obtain optimum grain size. The underlying critical issue is that the actual scanned volume of the test portion is small; e.g. with aluminium electrolyte the penetration depth of the x-ray beam is less than 2 mm and the quantitative analysis improves with correct counting statistics. For a diffractogram the optimum grain size is 5 - 10 μm .

Sources of Information - Phase Data - Principles

DES Consulting - David E. Simon

MDI Materials Data Inc. -

Anode Cover Material - ACM



Pure carbon does not burn easily; fairly inert to 500 °C - but cells operate at 960°C - ACM shields from air burnoff

Anode Cover Material - ACM

A 500 000 tonne/year aluminium plant will process 200 000 tonne/year ACM!

Show video - anode setting and removing

Primary ACM

Mixture of secondary ACM and new alumina, 2/3 bath, 1/3 alumina

Secondary ACM

Material removed from top of spent anodes or butts

Anode Cover Material - How does it work?

Quite sophisticated, actually

Fresh alumina is 95+ % transition aluminas

gamma, theta, kappa

In the cell the transition aluminas are converted in situ to a grid or network of alpha -alumina platelets

The network is supported by bath material, and this composite is strong, physically, and chemically fairly resistant to washing away by the electrolyte than bath alone

Composition - Major Elements ACM

Al	31.867 - Range [25.300 to 39.000]
F	29.871 - Range [19.170 to 40.730]
O	18.683 - Range [10.400 to 27.800]
Na	15.467 - Range [10.000 to 21.400]
Ca	1.525 - Range [1.000 to 2.200]
C	0.754 - Range [0.210 to 1.730]

To estimate Al₂O₃ from oxygen, multiply by 2

ICP, XRF, Leco -O, Leco-C, Sintanglyzer -F

X-Ray Laboratories in Hydro Aluminium

The operational labs has XRD.

Electrolyte samples are 100 -200 per day; fast analysis, high throughput; high intensity, moderate precision

We need scans with good resolution, and this is from a study to determine if the grinding step can be optimised for resolution

Anode Cover Material - Issues

What composition is optimal?

How to analyse?

Primary ACM has more transition alumina than already used ACM, but is more expensive - how much to add, how much to recycle

There is a lot of secondary once-used ACM - must be reused

Studies are running, and the ACM is being analysed in more detail

Here is where Rietveld XRD quantification comes in

Swing Mill and McCrone Microniser

Swing Mill - grinding time in seconds 8 - 15 - 30 seconds

Test portion 12 gram, dry, initial grain size < 1 mm

Wolfram carbide covered steel ring -and-puck run in Herzog machine

McCrone - grinding time in minutes 4 - 8 - 15 minutes

Test portion 0.6 gram, isopropanol slurry, grains < 0.4 mm

Sintered alumina grinding elements plus one Agate run

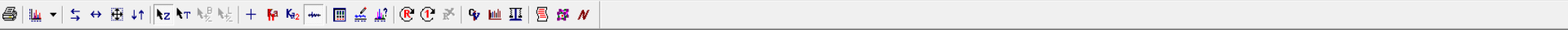


Observations

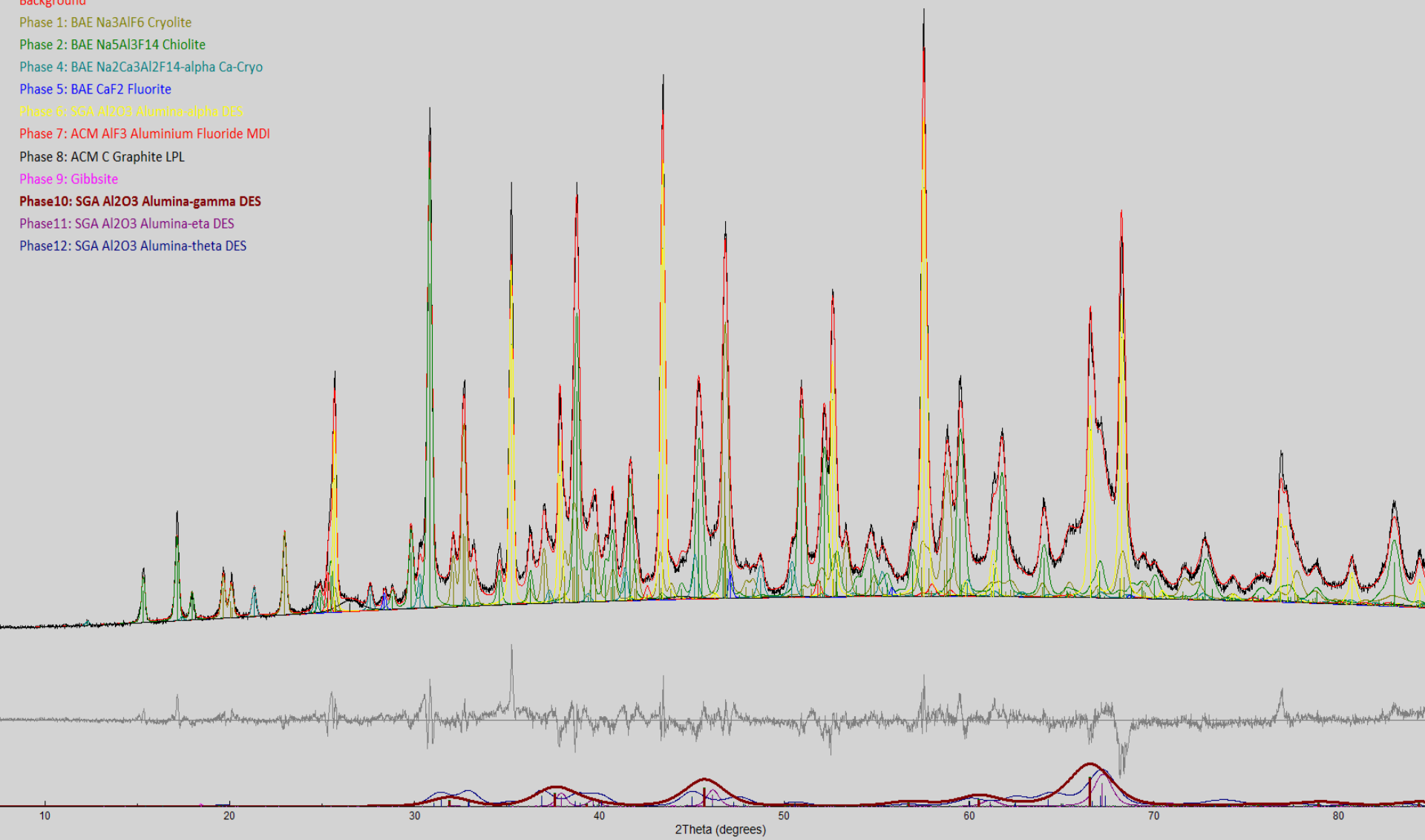
Already a visual inspection of diffractograms reveal differences

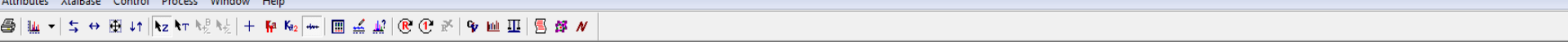
Twelve phases

Six major elements

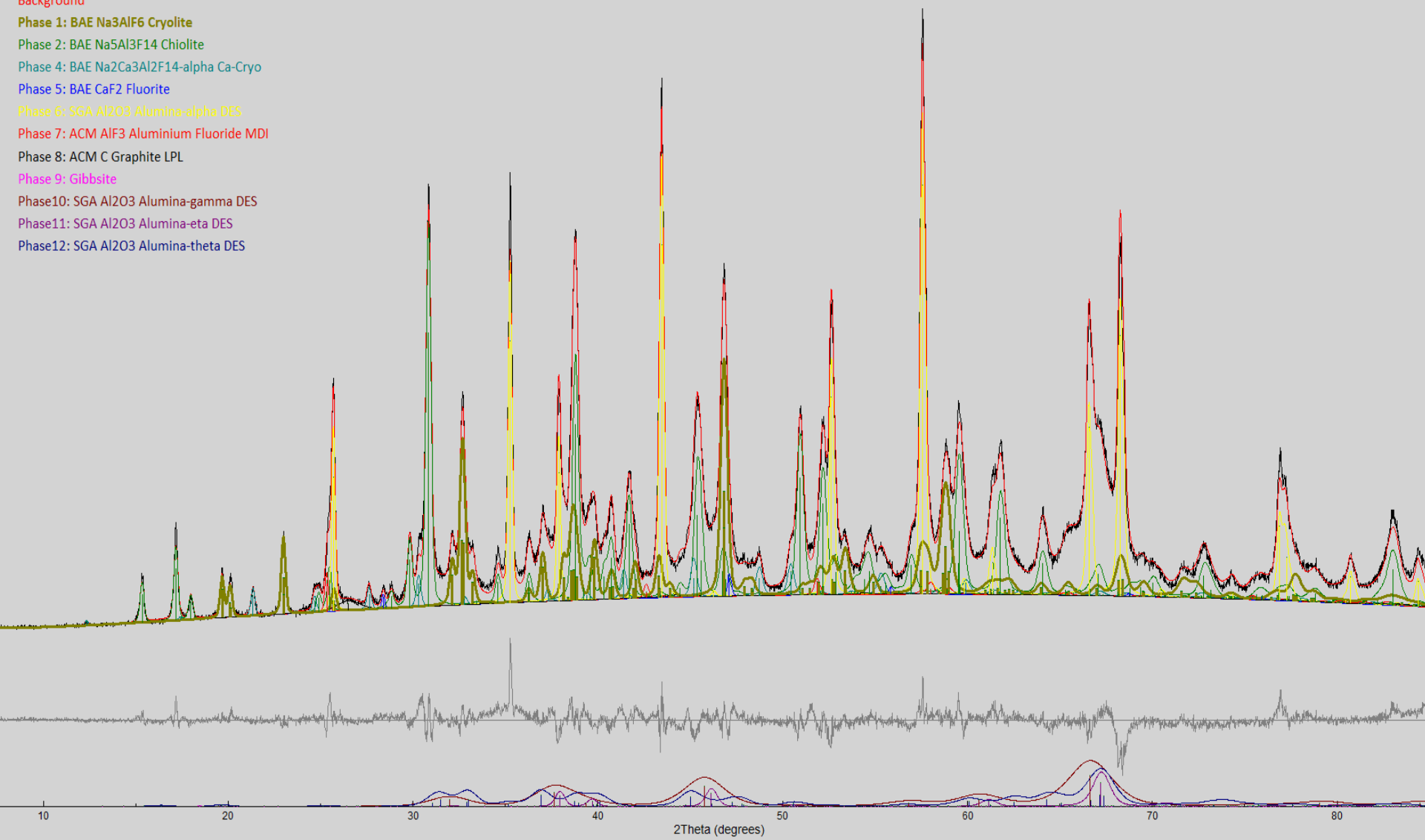


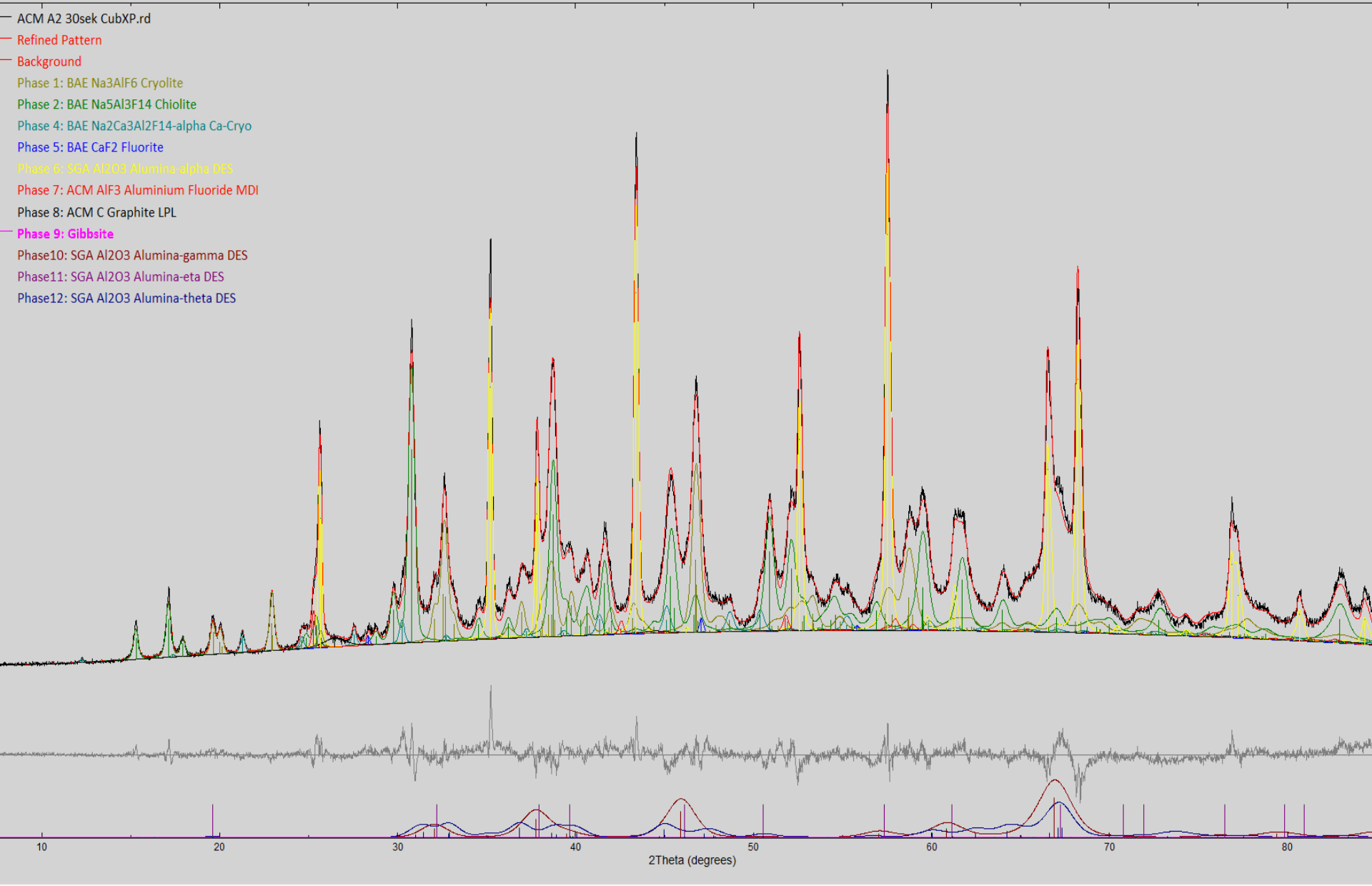
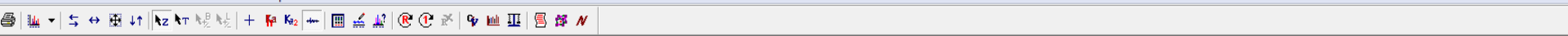
- ACM A2 08sek CubXP.rd
- Refined Pattern
- Background
- Phase 1: BAE Na3AlF6 Cryolite
- Phase 2: BAE Na5Al3F14 Chiolite
- Phase 4: BAE Na2Ca3Al2F14-alpha Ca-Cryo
- Phase 5: BAE CaF2 Fluorite
- Phase 6: SGA Al2O3 Alumina-alpha DES
- Phase 7: ACM AlF3 Aluminium Fluoride MDI
- Phase 8: ACM C Graphite LPL
- Phase 9: Gibbsite
- Phase10: SGA Al2O3 Alumina-gamma DES**
- Phase11: SGA Al2O3 Alumina-eta DES
- Phase12: SGA Al2O3 Alumina-theta DES

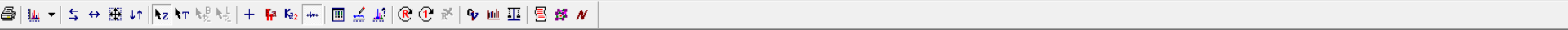




- ACM A2 15sek CubXP.rd
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- Background
- Phase 1: BAE Na3AlF6 Cryolite
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- Phase 4: BAE Na2Ca3Al2F14-alpha Ca-Cryo
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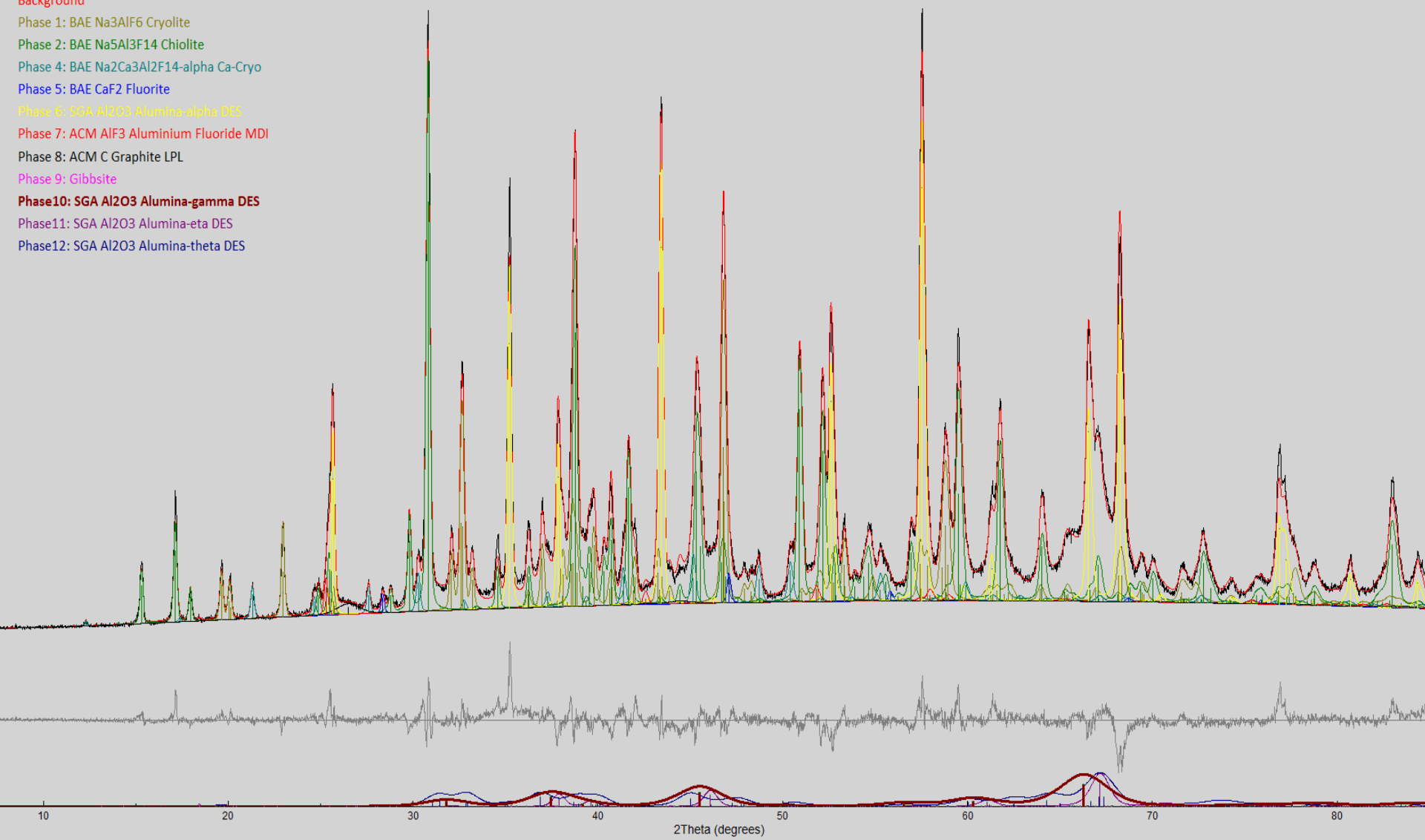


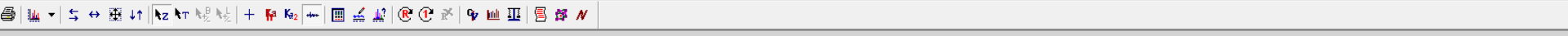




ACM 07 A2 McCrone 04 CubXP.rd

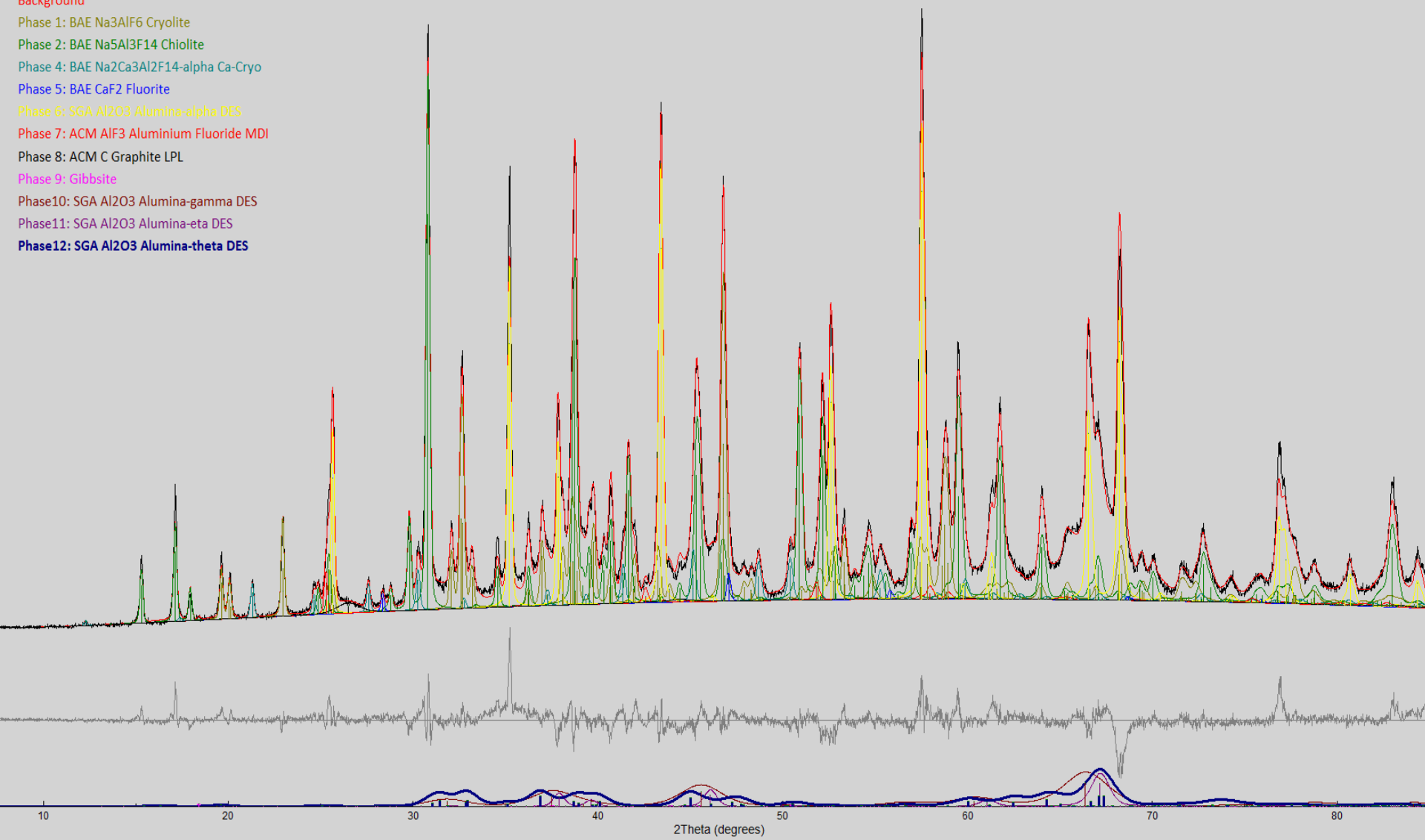
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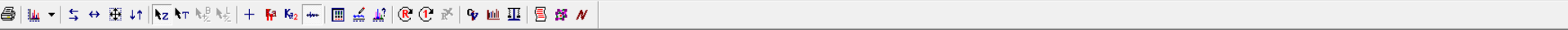




ACM 08 A2 McCrone 08 CubXP.rd

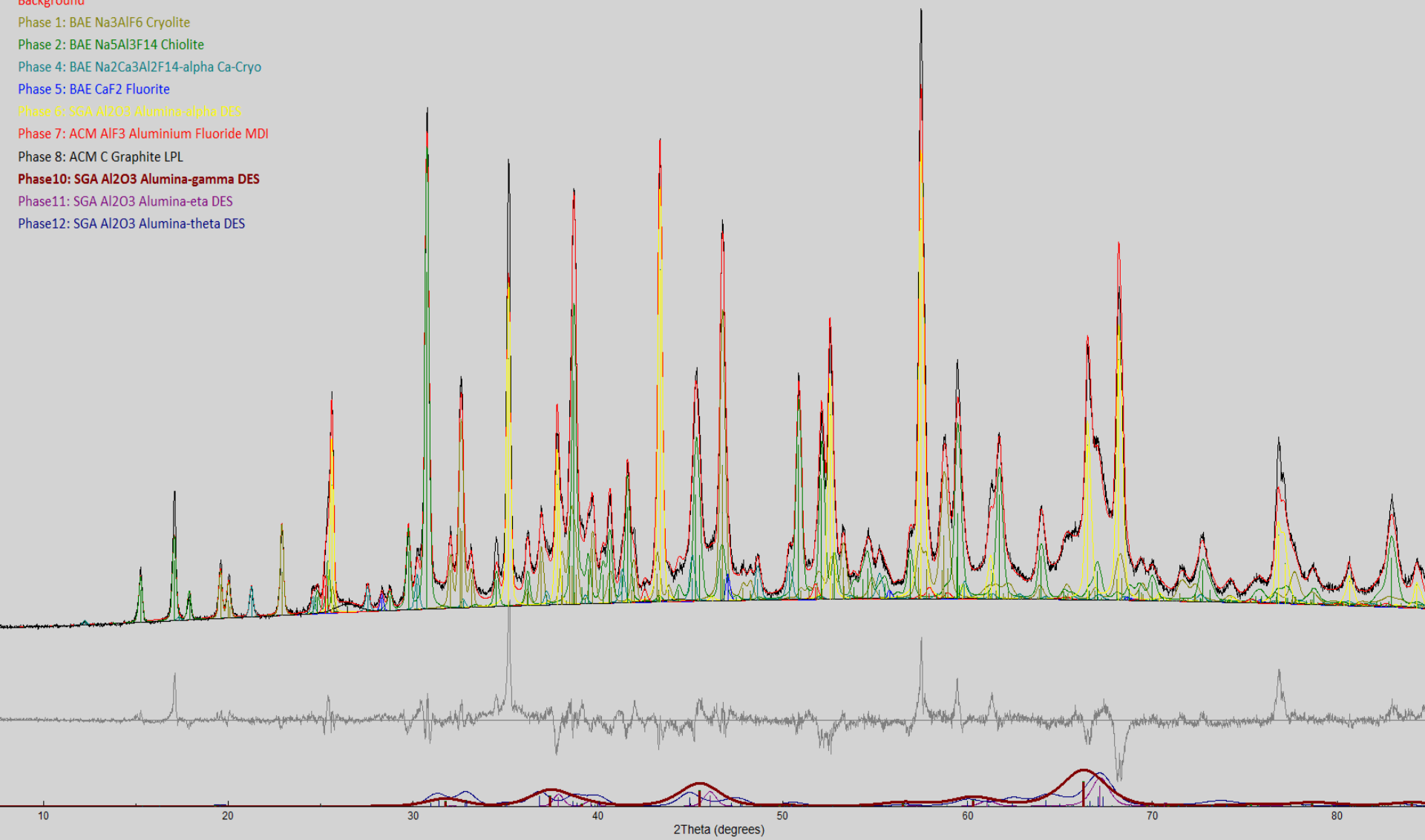
- Refined Pattern
- Background
- Phase 1: BAE Na3AlF6 Cryolite
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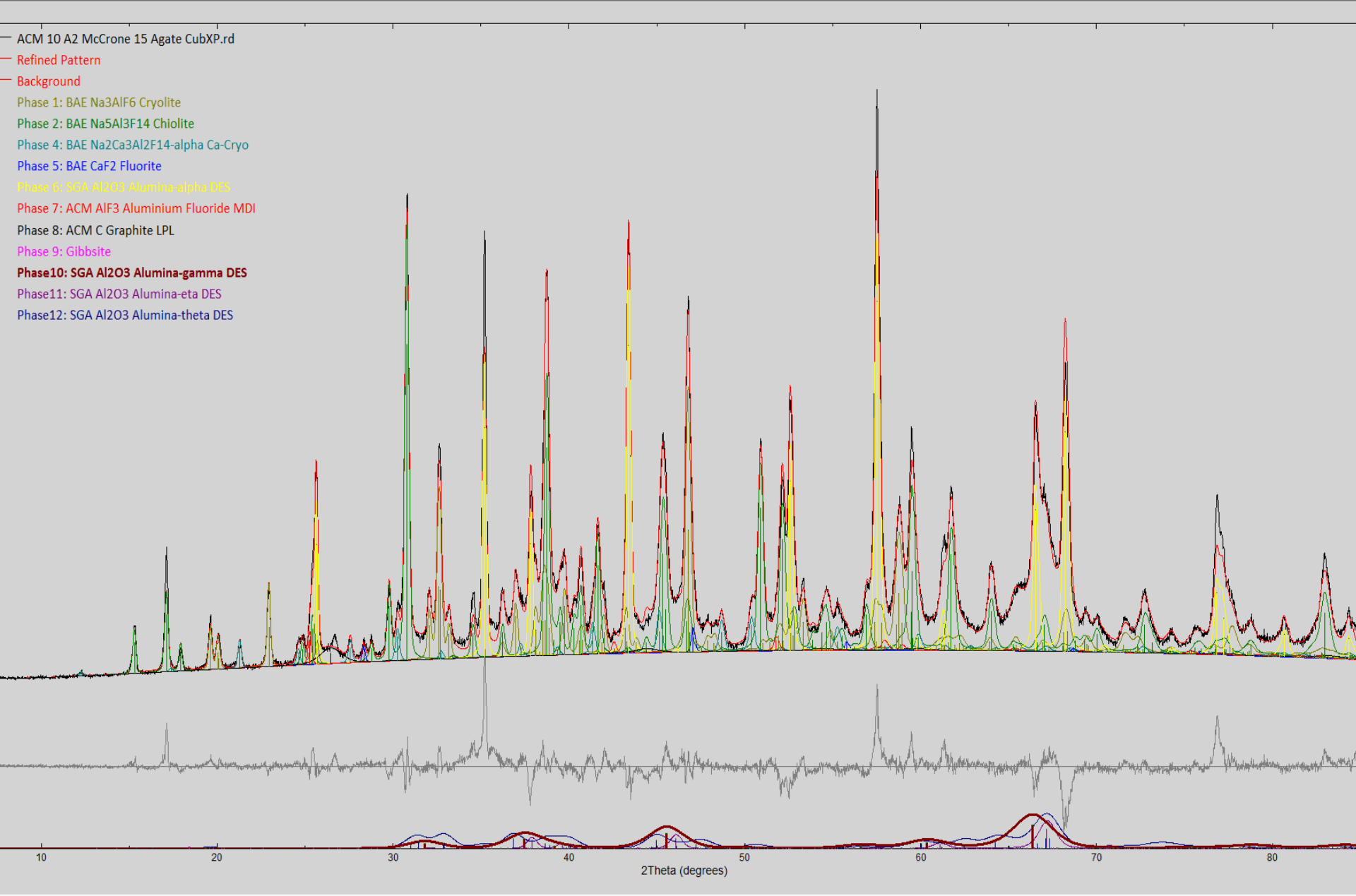




ACM 09 A2 McCrone 15 CubXP.rd

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Swing Mill and McCrone Microniser

Swing Mill 8 - 15 - 30 seconds, increasing FWHM showing damage to fluorides while all aluminas retains intensity

McCrone - grinding time 4 - 8 - 15 minutes, moderate increasing FWHM for the fluorides, also alpha peaks increases similarly .

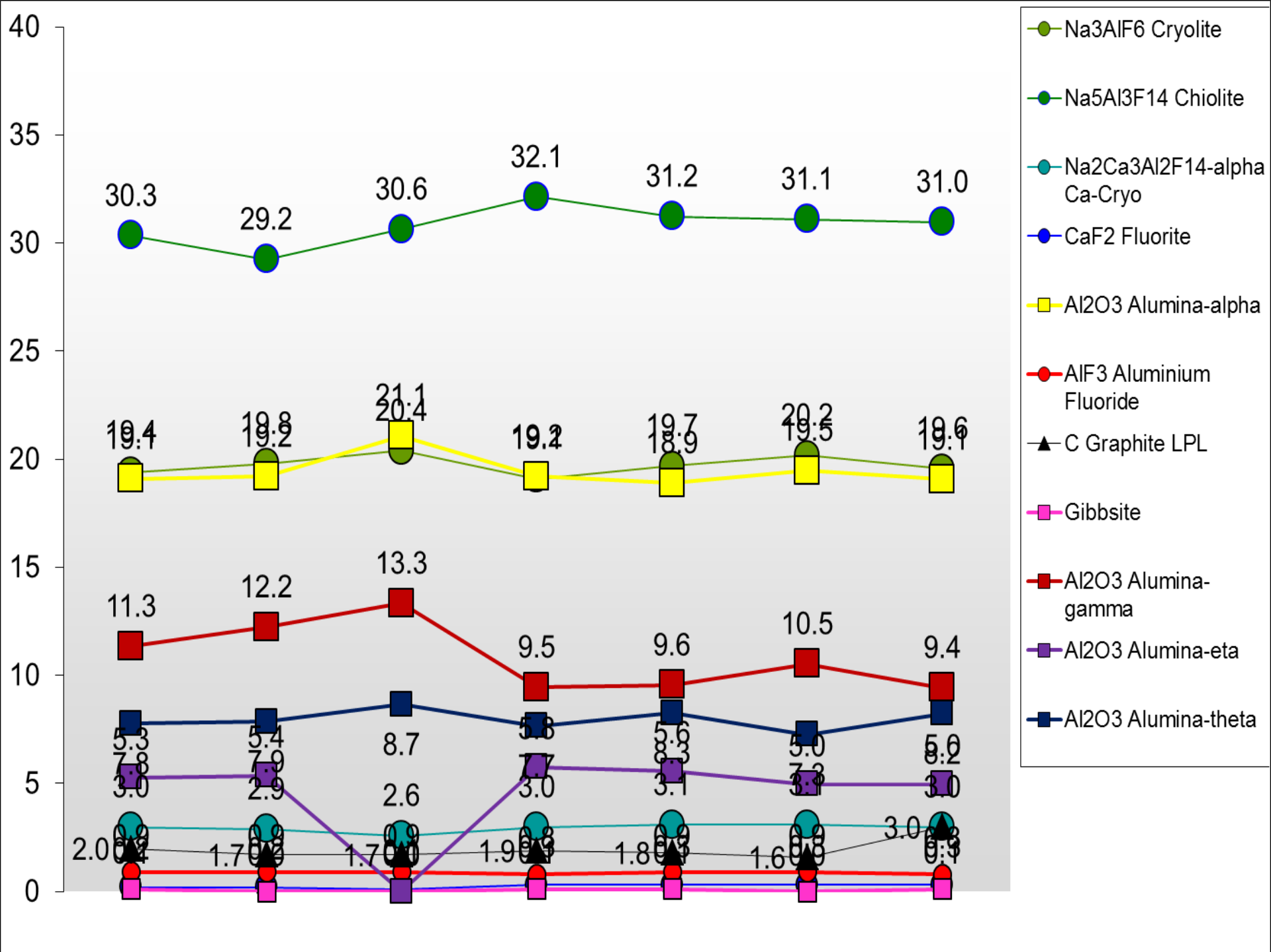
Some alpha peaks indicate orientation or other effect

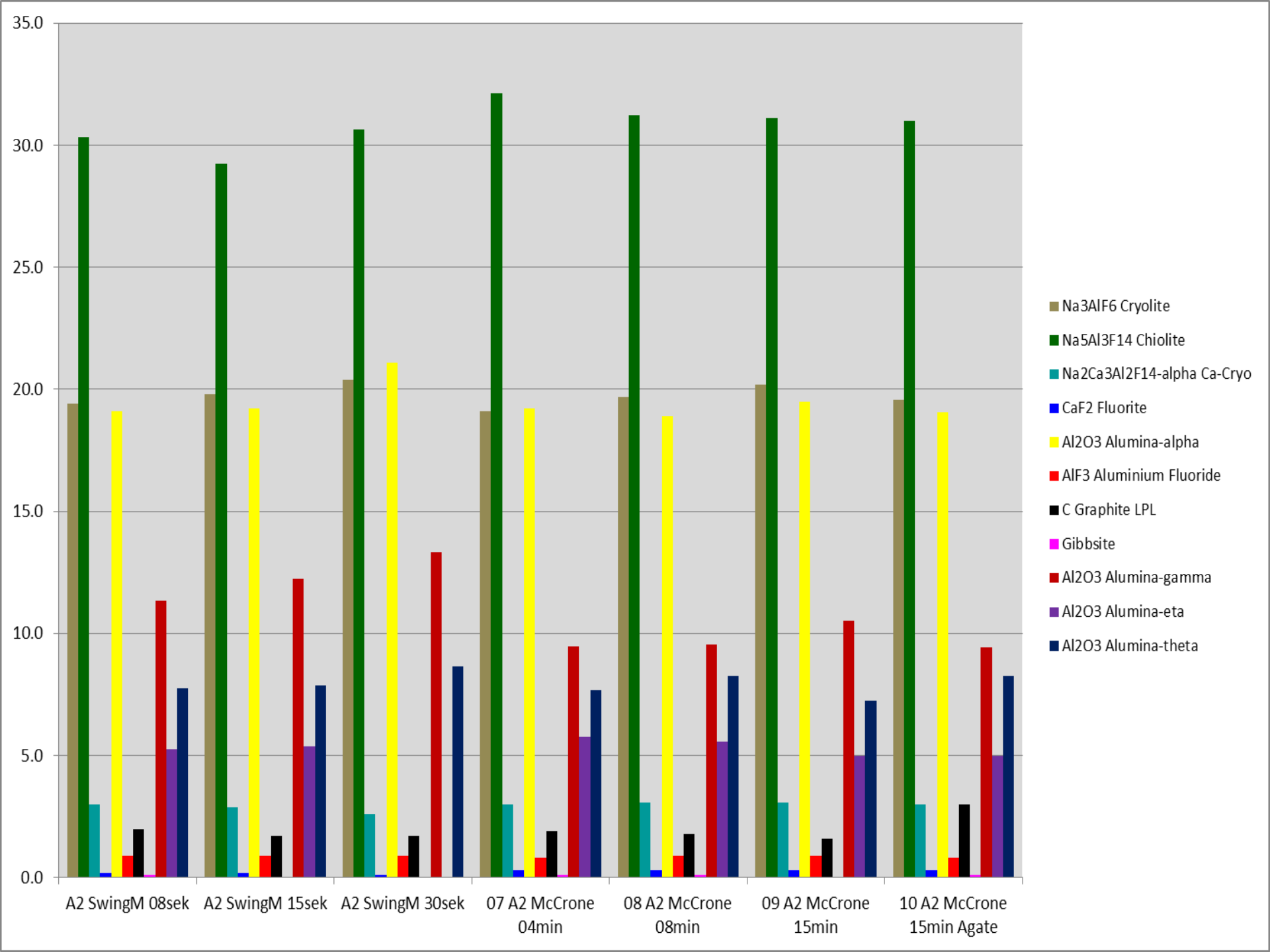
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Swing Mill 8 - 15 - 30 seconds, increasing FWHM showing damage to fluorides while all aluminas retains intensity

McCrone - grinding time 4 - 8 - 15 minutes, moderate increasing FWHM for the fluorides, also alpha peaks increases similarly.

Increasing FWHM means, if used as calibration materials at different sites - to get a valid calibration, all calibration materials must have same sample prep as routine samples





Fluorine, F - Compared		Sintalyzer	Rietveld	Sodium, Na - Compared		ICP	Rietveld
			XRD				XRD
		wt%	wt%			wt%	wt%
A2 SwingM 08sek		27	30	A2 SwingM 08sek		14.2	14.2
A2 SwingM 15sek		27	30	A2 SwingM 15sek		14.2	14.1
A2 SwingM 30sek		27	31	A2 SwingM 30sek		14.2	14.6
07 A2 McCrone 04min		27	31	07 A2 McCrone 04min		14.2	14.6
08 A2 McCrone 08min		27	31	08 A2 McCrone 08min		14.2	14.5
09 A2 McCrone 15min		27	31	09 A2 McCrone 15min		14.2	14.7
10 A2 McCrone 15min Agate		27	31	10 A2 McCrone 15min Agate		14.2	14.4
Average		27.4	30.8	Average		14.2	14.4
Comment				Comment			
Sintalyzer is by electrochemical fluoride titration				ICP - wet chemical elemental analysis			
XRD is based on the phase concentrations				XRD is based on the phase concentrations			
Calcium, Ca - Compared		ICP	Rietveld				
			XRD				
		wt%	wt%				
A2 SwingM 08sek		1.30	0.84				
A2 SwingM 15sek		1.30	0.82				
A2 SwingM 30sek		1.30	0.69				
07 A2 McCrone 04min		1.30	0.89				
08 A2 McCrone 08min		1.30	0.92				
09 A2 McCrone 15min		1.30	0.91				
10 A2 McCrone 15min Agate		1.30	0.89				
Average		1.30	0.91				
Comment							
ICP - wet chemical elemental analysis							
XRD is based on the phase concentrations							

Carbon, C - Comparing				Oxygen, O - Comparing							
Leco-C		Rietveld		Leco-O		Rietveld					
		XRD				XRD					
wt%		wt%		wt%		wt%					
A2 SwingM 08sek		1.03		2.0		A2 SwingM 08sek		19.7		20.5	
A2 SwingM 15sek		1.03		1.7		A2 SwingM 15sek		19.7		21.0	
A2 SwingM 30sek		1.03		1.7		A2 SwingM 30sek		19.7		20.3	
07 A2 McCrone 04min		1.03		1.9		07 A2 McCrone 04min		19.7		19.9	
08 A2 McCrone 08min		1.03		1.8		08 A2 McCrone 08min		19.7		20.0	
09 A2 McCrone 15min		1.03		1.6		09 A2 McCrone 15min		19.7		19.9	
10 A2 McCrone 15min Agate		1.03		3.0		10 A2 McCrone 15min Agate		19.7		19.7	
Average		1.0		1.9		Average		19.7		20.2	
Comment				Comment							
Leco-C is direct measurement				Leco-O is direct measurement							
XRD is calculated from the phases (only graphite phase)				XRD oxygen is based on the phase concentrations							
Aluminium, Al - Comparing				Alumina, Al2O3 - Comparing							
ICP		Rietveld		From Leco-O		Rietveld					
		XRD				XRD					
wt%		wt%		wt%		wt%					
A2 SwingM 08sek		33		31		A2 SwingM 08sek		41.9		43.6	
A2 SwingM 15sek		33		32		A2 SwingM 15sek		41.9		44.7	
A2 SwingM 30sek		33		31		A2 SwingM 30sek		41.9		43.1	
07 A2 McCrone 04min		33		31		07 A2 McCrone 04min		41.9		42.2	
08 A2 McCrone 08min		33		31		08 A2 McCrone 08min		41.9		42.4	
09 A2 McCrone 15min		33		31		09 A2 McCrone 15min		41.9		42.2	
10 A2 McCrone 15min Agate		33		31		10 A2 McCrone 15min Agate		41.9		41.8	
Average		33.1		31.2		Average		41.9		42.8	
Comment				Comment							
ICP - wet chemical elemental analysis				Gravimetrisk faktor er 102.0 / 48.0.							
XRD aluminium is based on the phase concentrations				XRD er sum alfa-, gamma-, theta-alumina,							

Comparison with Leco -O, ICP, Sintalyzer -F

The Rietveld XRD showed very good agreement with alumina calculated from Leco -O

Na by ICP was close

F by Sintalyzer was 10% off

Al by ICP was 5% off

Comparison with Leco -O, ICP, Sintalyzer -F

The Rietveld XRD showed very good agreement with alumina calculated from Leco -O

Na by ICP was close

F by Sintalyzer was 10% off

Al by ICP was 5% off

Some work needed on C phase model and CaF_2 Fluorite

Very little variation between sample prep methods on element level

Conclusions

Rietveld quantitative of anode cover material functioned well with oxygen close to Leco -O values

The Swingmill running 8 - 15 - 30 seconds showed increasing overgrinding of the fluorides - alumina was little changed

The McCrone running 4 - 8 - 15 minutes showed less peak widening than swing milling 8 seconds and little increase

Agate grinding elements were the same as sintered alumina

McCrone gave phase sums closer to Leco -O than swingmill

Some peaks not well modelled - more information available in this system



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