Comparison of Pilot Anode Production and Testing Between Two Laboratories and Ability to Simulate Full Scale Anodes

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Abstract
Simulating industrial quality anodes at pilot scale is challenging. In the current study, Hydro Aluminium and RAIN Carbon prepared multiple sets of identical aggregate recipes and made pilot anodes in two different laboratories. Hydro Aluminium Technology operates two pilot lines at their Årdal facility in Norway and RAIN Carbon operates a pilot line at their Castrop-Rauxel facility in Germany. Pilot anodes 4-6 kg in weight were produced using two different coke blends at several levels of pilot anode settings. RAIN Carbon supplied 24 sets of a baseline aggregate using an industrial coke blend and crushed baked anode scrap. Hydro Aluminium supplied 32 sets of coke and butts fractions from a full-scale anode plant. Excerpts of the results are presented and compared for the green anode production and baking processes and general anode core analysis results. The use of pilot anode testing for simulation of full scale anodes is discussed.

Keywords: Anode Plant, Pilot Scale Testing, Comparative Study, Anode Production, Anode Analysis.

1. Introduction

Hydro Aluminium and RAIN Carbon (hereafter Hydro and RAIN) have a long history of cooperation, from general customer support by RAIN to scientific studies and co-authorship of research papers. Hydro is an integrated aluminium producer with extensive research activities including research on carbon raw materials for anodes. RAIN is a raw materials supplier to several industries including aluminium production where the main materials are petroleum coke and coal tar pitch. Both companies operate pilot scale anode testing facilities. Since 2015, a technical cooperation has developed with the intent of working jointly on comparative studies of raw materials. Hydro operates two pilot lines at the Primary Metal Technology (PMT) facility in Årdal, Norway. [1] RAIN operates a pilot line at their Castrop-Rauxel facility in Germany [2]. There are not many pilot anode testing facilities, and every line probably has unique features. Conducting parallel studies and sharing results between different pilot lines presents an excellent learning and benchmarking opportunity. This paper will describe the results of such a study between Hydro and RAIN.

1.1. Full Scale or Pilot Scale?

Testing of cokes and binders in a full-scale anode plant is feasible and will give the most realistic industrial results. However, continuous stable operation of an anode plant will always take priority over any form of testing. On this basis, testing at a pilot-scale facility is preferable. Other significant advantages of pilot-scale are lower cost, shorter testing feedback and far greater versatility in experimental designs.

1.2. Comparative Pilot Anode Studies

A first study was run to establish a methodology for sharing material sets, and to see the effect of parallel production at the two facilities with the same calcined petroleum coke (CPC) aggregate and binder. This data set is hereafter termed "Set1" anodes. The Set1 study was also used to compare analysis results. A smaller, second study was run where a different aggregate and binder was shared and used (Set2).

The Set1 aggregate was prepared by RAIN and the Set2 aggregate by Hydro using similar procedures. Two different binders produced by RAIN were used in the studies.

Table 1. Raw materials Set1 and Set2 tested at each site. Production temperatures (Tmix) were adapted to match the binder softening point. Tmix was the green mixing target.

	Anodes	Aggregate	Binder	Tmix [°C]	Binder Levels [wt%]
Set1	8	RAIN Baseline Coke	BX112M	180	13.5, 14.0, 14.5, 15.0
Set2	3	Hydro Paste Plant Fractions	BX125M	195	13.5, 14.0, 14.5

1.3. Requirements for Good Comparison

Several steps are critical for a successful comparative test of pilot scale anodes.

Equal Aggregate: Preparation of raw materials to ensure an identical set of aggregates was achieved by splitting to exact portions ready for adding to the mixer, for each fraction for both Set1 and Set2 aggregates.

Pilot Production: Understanding which settings in production must be the same at the sites - the anodes were produced under regular pilot production conditions at each site, except temperatures for preheat, mixing and forming which were adapted to the level suitable for the binders used.

Analysis Round Robin (RR): Participants must have confidence that anode test methods and results are comparable at both laboratories since the analysis results determines our understanding of the anode quality. An analysis RR was integrated in the first pilot anode study. At each site, a pair of anodes were made for every setting, and after baking, one anode from each setting pair was sent to the other laboratory for coring and analysis. When showing charts, this makes four points of results that should be as close as possible.

2. Experimental

2.1. Comparing the Two Pilot Scale Lines

An overview of the two lines is shown in Table 2. The Hydro pilot line in Årdal has been in operation with a vacuum vibroformer since 2005 with over 1600 pilot anodes produced. RAIN's relatively new pilot anode facility has been in operation in its current form since 2013 with just over 800 anodes produced. All of RAIN's aggregate preparation work is done at the RAIN central lab in Lake Charles, USA.

Table 2. Two pilot anode lines compared. Binder levels, mixer configuration, mixer energy input and the temperatures depend on the raw materials used.

Equipment	Hydro Aluminium AS Primary Metal Technology, Årdal	RAIN Carbon Castrop Rauxel
Name Line/Mixer	R-02 Line	RV-02
Pilot Anode Mass	3.80 kg	5.2-5.3 kg
Pilot Anode Size	ø130x178 mm, height approximate	ø146x200 mm, height approximate
Mixer	Eirich R-02, upright – with heating, maximum reached 260 °C	Eirich RV-02E (10 l), upright - with IR heat source up to 300 °C
Mixer Settings	Depends on binder, for 125M SP, target mix end-temp 195 °C - density target is industrial anode value	Depends on binder. For 112M SP, regular mixing temperature is 180 °C
Mixer Energy Input	PressDown rotor, 3.0 minute mixing time, tip speed 9.0 m/s	LiftUp rotor, 10.0 minute mixing, tip speed 12.0 m/s
Forming	Vibroformer, Wilkening design with 50 Hz frequency – up to 200 °C Evacuation usually at 24 mbar Temp. 55-70 °C over softening point	Hydraulic Press - (double action pistons) up to 320 °C No evacuation Temp. 15 to 25 °C above softening point
Reference Binder	BX125M	BX112M
Baking Furnace	Norwegian custom design, up to 16 anodes	Same manufacturer and similar design to Hydro Aluminium furnace
Baking Level	Target 1260 °E, can be used up to 1380 °E	Normally in the 1240-1260 °E range, up to 1380°

2.2. Experimental – List of Analyses Made

The study involves several types of analysis, including characterization of the raw materials, logging of values during the production and, most importantly, the routine analysis of anode quality parameters in Table 3. These properties are used when comparing pilot anodes with anodes produced at full scale and are central in the presentation of results to plant operations.

Table 3. Anode core analysis: Analysis available and analysis made at both sites for the analysis RR – blank means not made, and "no"=not available.

Analysis	Hydro	RAIN	Analysis RR
Hydro R.CO_2 [mg/cm²h]	√	no	
Hydro DustIndex [rel%]	√	no	
Hydro Dust.CO_2 [mg/cm²]	√	no	
Hydro R.Air [mg/cm²h]	√	no	
RDC Reac.CO2.CRR [%]	√	√	√
RDC Reac.CO2.CRD [%]	√	√	√
RDC Reac.CO2.CRL [%]	√	√	√
Density d [g/cm³]	√	√	√

Spec. El. Resistance SER [μΩm]	√	√	√
Young's Modulus YM [MPa]	√	√	√
Cold Crushing Strength CCS [MPa]	√	√	√
Permeability [nPm]	√	√	√
Thermal Expansion CTE [μm/mK]		√	
Flexural Strength [MPa]	no	√	
Thermal Conductivity TC [W/mK]	√		

2.3. Production Monitoring

- In addition to routine analysis of the baked anode cores, Hydro and RAIN track various additional parameters like green apparent density, volume shrinkage, binder coke yield.
- Green paste extraction and sieve analysis of the aggregate after mixing was done to compare changes due to crushing during mixing. This work was done at the PMT Laboratory in Porsgrunn. [3]

3. Production

3.1. Binder Properties

Some of the binder properties are listed in Table 4 with ISO standard designation and the DIN designation used by RAIN. "SPM" is Softening Point Mettler.

Table 4. Binder analysis results.

Property		BX112M	BX125M	ISO	DIN
Softening Point, SPM	[°C]	112	128.6	ISO 5940-2	DIN 51920
Toluene Insoluble, TI	[%]	25.7	28.8	ISO 6376:1980	DIN 51906
Quinoline Insoluble, QI	[%]	5.1	7.9	ISO 6791:1981	DIN 51921
Alcan Coking Value	[%]	57.6	62.4	ISO 6998:1997	DIN 51905

3.2. Recipes and Aggregate

RAIN supplied the Set1 aggregate based on an industrially used coke blend and crushed down baked anode scrap for use as butts. Table 5 gives the list of fractions received. Some similarities and differences are obvious in the two sets with Set2 shown in Table 9.

Table 5. RAIN aggregate used for Set1 anodes. BMP is ball mill product.

RAIN Carbon Baseline Coke A	Range (mm)	Mass fraction (wt%)
Butts 8-4.75	8-4.75	13.0
Butts 4.75-1.7	4.75-1.7	7.0
Coke 8-4.75	8-4.75	10.0
Coke 4.75-1.7	4.75-1.7	15.0
Coke 1.7-0.85	1.7-0.85	12.0
Coke 0.85-0.30	0.85-0.30	10.0
Coke 0.30-0.15	0.30-0.15	7.0
Coke BMP (~4500 Blaine)	-0.15	26.0

Hydro prepared the Set2 aggregate sets using the recipe in Table 6. The butts are regular returned and crushed-down butts originating at several Hydro-smelters in Norway. The "N" in "N-Butts" and "N-Coke" designations were random letters.

Table 6. Hydro aggregate for Set2 anodes.

Fraction	Range (mm)	Mass fraction (wt%)
N-Butts 12-4.0	12-4 mm	12.1
N-Butts 4.0-0	4-0 mm	9.9
N-Coke 11-4	11-4 mm	14.7
N-Coke 1-4	4-1 mm	23.9
N-Coke 0-1	1-0 mm	14.5
N-Coke BMP	BMP	24.9

4. Results

4.1. Material Set1

Both x-axis and y-axis are harmonized and the same for Set1 and Set2 results. The Experimental Design for Set1 is shown in Table 7. The Set1 study was run with four binder levels in duplicate, giving two anodes per level. One from each level was shipped to the other laboratory for the analysis round robin.

Table 7. Experimental Design for Set1 anodes Example, light blue "H-R" anodes producer Hydro and analysis by lab RAIN. "EXTR" = extraction analysis.

Producer	Analysis Lab	13.5	14.0	14.5	15.0	<-- binder (wt%)
Hydro	Hydro	R04	R02 EXTR.	R06	R08	H-H.Set1
Hydro	RAIN	R03 ATE.644	R01 ATE.645	R05 ATE.646	R07 ATE.647	H-R.Set1
RAIN	RAIN	ATE.627 EXTR.	ATE.631	ATE.633 EXTR.	ATE.636	R-R.Set1
RAIN	Hydro	ATE.630	ATE.628	ATE.629	ATE.632	R-H.Set1

Chart Layout for Set1 Using Baked Density as Example

The Set1 charts have four curves, two from each participant. "H-H" anodes were made and analyzed by Hydro and the "R-R" anodes were made and analyzed by RAIN.

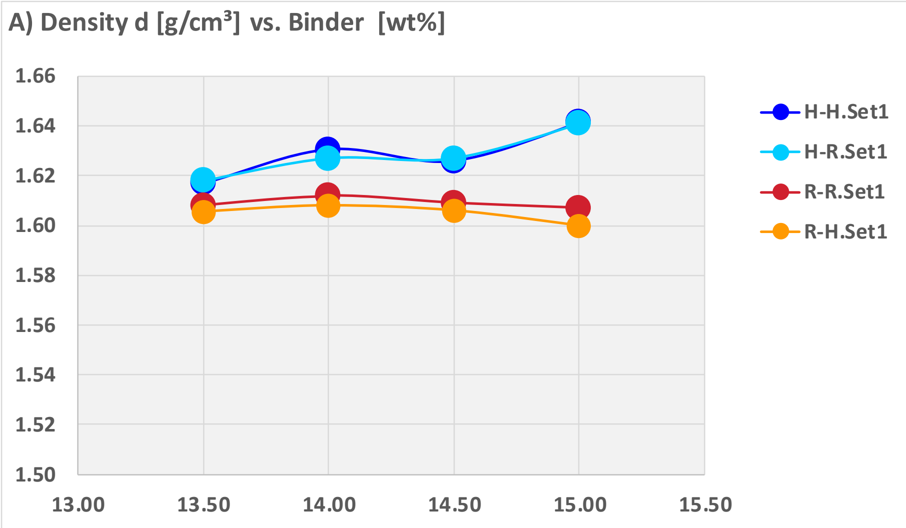

Figure 1. Baked density, Set1 anodes. Blue made by Hydro, red made by RAIN.

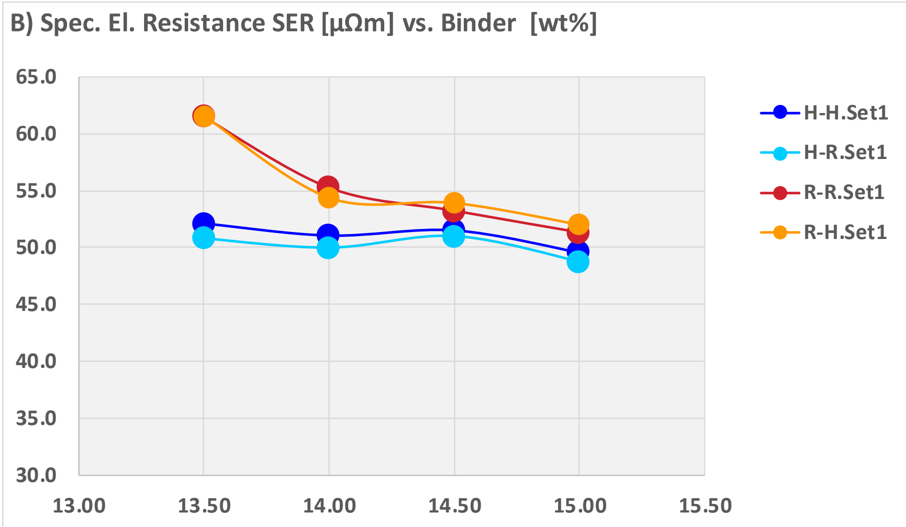

Figure 2. SER, Set1 anodes.

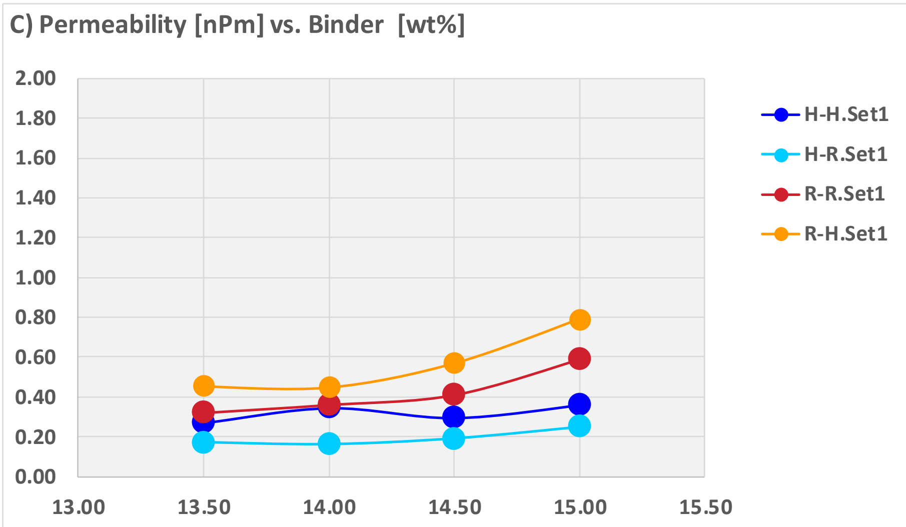

Figure 3. Permeability, Set1 anodes.

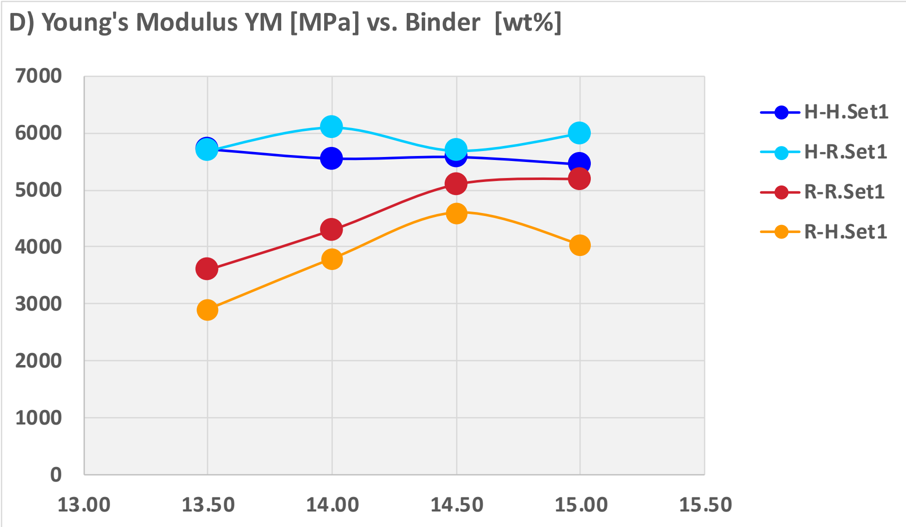

Figure 4. YM, Set1 anodes.

Looking at the charts, the overall impression is that trending is even and systematic. This is an indication of good repeatability in the production at both sites. The careful aggregate preparation and the well-defined production parameters helped with this, as did the care taken by the technicians making the anodes and the quality and up-keep of the test equipment at each facility.

There are differences in the charts which are easy to see as they, too, trend systematically across the binder levels. The trending was slightly more even for RAIN anodes than for Hydro anodes. The level and trending of the properties are compared in Table 8; for the anode quality comparison an "Industrial Range" is given.

Table 8. Evaluation of the anode results, Set1. "R"=RAIN and "H"=Hydro.

	Industrial Range	**PilotRR**	**RAIN Trend**	**Hydro Trend**	**Analysis RR**
Density [g/cm³]	low 1.55 high 1.63	comparable, trend different	curving through maximum	upward with binder	laboratories gave same results
SER [µΩm]	low 48 high 60	low different, but trending to similar	strong trend down	trend down	Laboratories gave same results
Perm [nPm]	low 0.3 high 1.3	comparable	slight upward	slight upward	laboratories differ, being looked into
YM [MPa]	low 3500 high 7000	low different, but trending to similar	strong up then flat	slight down	laboratories differ, being looked into

Repeatability

Without duplicates analyzed at the same laboratory, the actual repeatability could not be quantified. The results for density and SER, where the two blue and two red curves are nearly equal, are an indication that the duplicates were very close in quality.

4.2. Materials Set2

Both x-axis and y-axis are harmonized and the same for Set1 and Set2 results. The Experimental Design for Set2 is shown in Table 9. The Set2 study was run with three binder levels.

Table 9. Experimental Design for Set2 anodes. "H.Set2" means Hydro-produced at temperature-settings suitable for mixing end temperature 195 °C.

	Temp. Mix	Temp. Forming	13.5	14.0	14.5	<-- binder (wt%)
Hydro	195	174	R21	R22R34	R23	H.Set2
RAIN	195	174	ATE864	ATE865	ATE866	R.Set2

Chart Layout for Set2 Using Density as Example

The layout for Set2 is shown in Figure 5. The blue cloud shows full scale anode results extracted from the Hydro Anode Data (HAD). HAD is a Big Data compilation of logged and measured anode information.

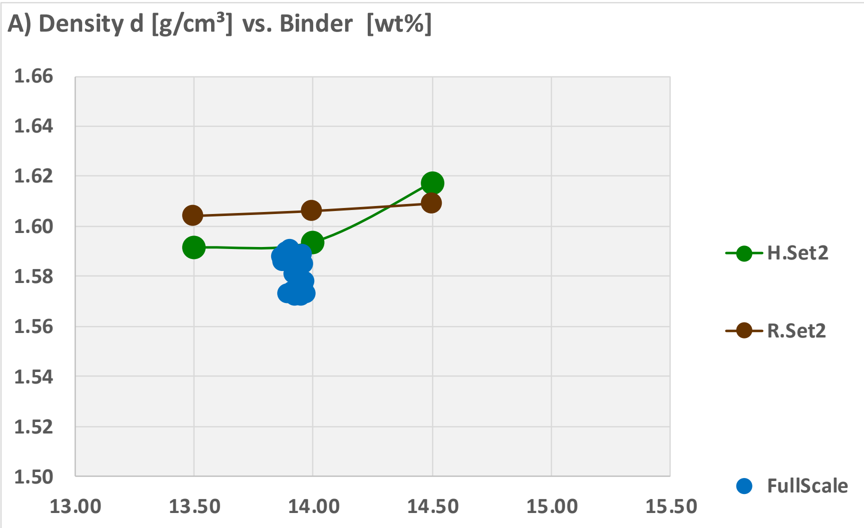

Figure 5. Baked density for the Set2 anodes. Green made by Hydro Aluminium, brown by RAIN Carbon. "FullScale" is the same aggregate at the Hydro anode plant.

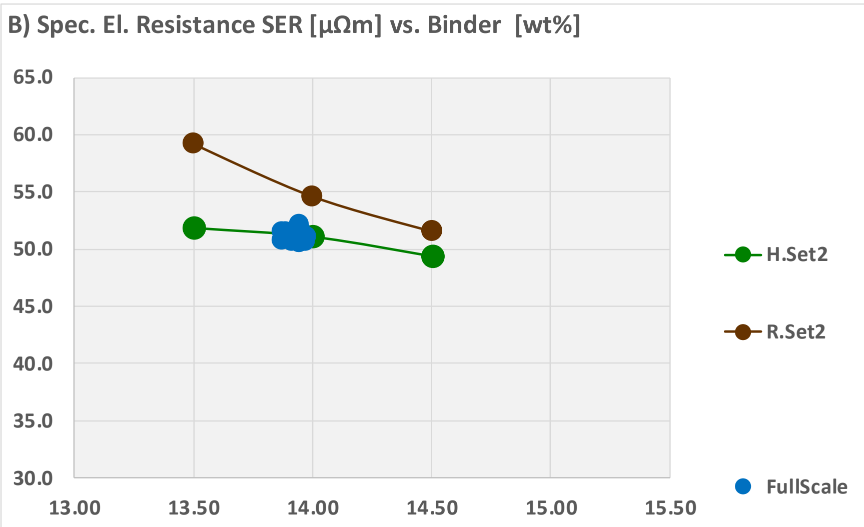

Figure 6. SER for the Set2 anodes.

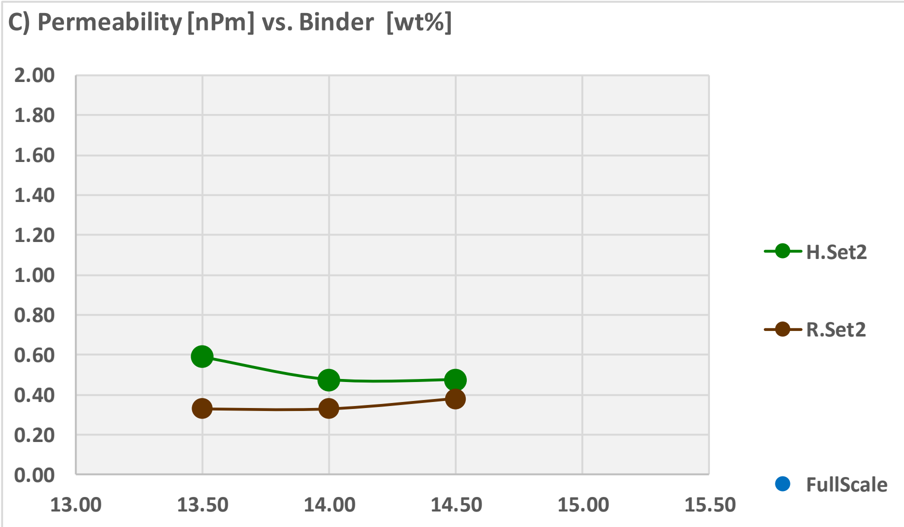

Figure 7. Permeability for the Set2 anodes. No Full Scale data due to the Permeability instrumentation being out of service at the time of testing.

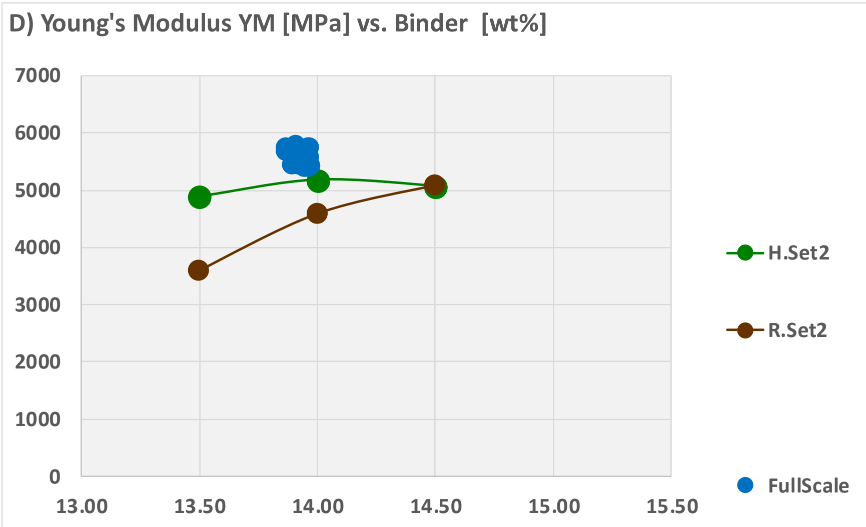

Figure 8. YM for the Set2 anodes.

The Hydro pilot line is tuned to simulate the anode quality at the "Full Scale" Hydro anode plant for the Set2 type of material which originated at that paste plant. Good agreement is seen between pilot scale and full scale.

Looking at the charts, the Set2 anodes showed systematic and very even trending with the binder level at both sites, as did the Set1 anodes. In Table 10, the anodes are compared. The RAIN and Hydro property levels are comparable for a binder level of 14.0 wt% to 14.5 wt%, and most similar for anodes with 14.5 wt%.

Table 10. Evaluation of the anode results, Set2. "R"=RAIN and "H"=Hydro.

		PilotRR	RAIN Trend	Hydro Trend
Density [g/cm³]		Same trend, different gradient	Slight, even upward	Upward, increasing with binder level
SER [μΩm]		Same trend, different gradient	Steep down	Even down
Perm [nPm]		Comparable	Even, slight upward	Even, possible minimum
YM [MPa]		Trending to same level	Even upward	Even, possible maximum

4.3. Extraction Analysis to Determine the Change in the Aggregate

The effect of the mixing on the post-mixing grain size distribution was determined by extraction analysis of green paste collected at both sites. One green paste prepared by Hydro and two made pastes prepared by RAIN were tested, Table 11.

Table 11. Cumulative grain size distribution as "percent greater than". NEW is the initial Set1 aggregate.

	+8mm [%]	+4mm [%]	+2mm [%]	+1mm [%]	+.25mm [%]	Bottom [%]
NEW (all)	4.6	25.0	40.9	52.9	68.0	32.0
Hydro R02	0.0	15.2	27.5	39.4	58.0	42.0
RAIN ATE629	0.0	13.5	27.5	42.2	60.7	39.3
RAIN ATE627	0.0	15.8	29.0	43.1	61.7	38.3

The NEW and crushed aggregate is compared in three panes in Figure 9 with the upper pane for the full aggregate, middle pane for mid-size grains and lower pane -1 mm grains.

- Upper pane: For coarse +4 mm, comparable loss at Hydro and RAIN with 10 wt% decrease. For mid-size only, Hydro aggregate decreases.
- Middle pane: A difference, with decrease for both of the 4-2 mm grains, but a small increase of 2 wt% for the RAIN aggregate.
- Lower pane: Both saw increase in fines, for the Hydro aggregate a greater increase in the finest tail.

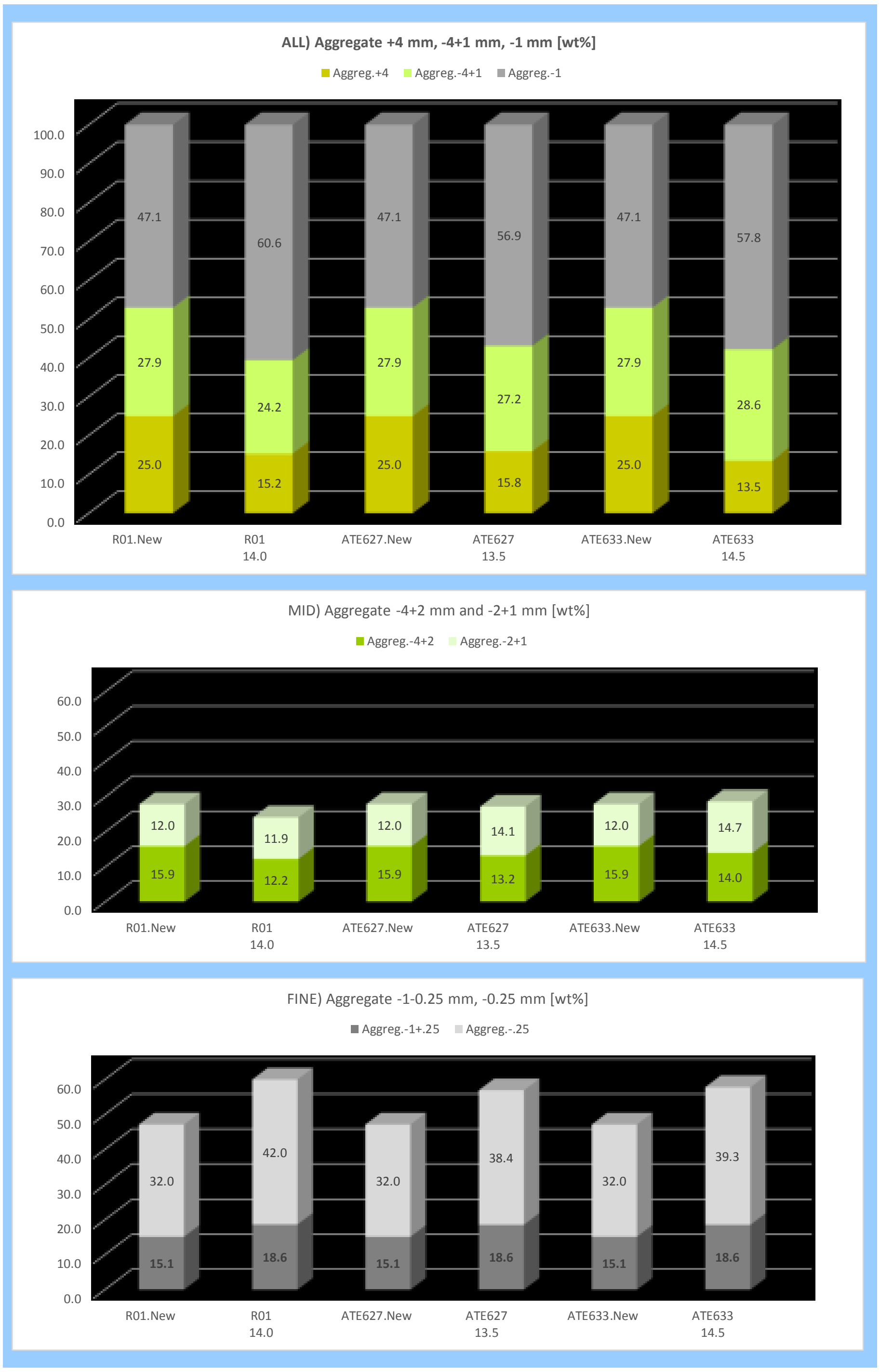

Figure 9. Comparing NEW aggregate to aggregate after mixing and binder extraction. The "New" aggregate is based on RAIN Baseline Coke recipe, see Table 5.

The extraction analysis showed a significant amount of crushing for both pilot line mixers at a comparable level to what is seen in full scale mixing. Both Pilot line mixers will see considerable impact crushing which will increase with tip speed and mixing time. Even though the Hydro mixer had a shorter mixing time and slower rotor speed than the RAIN mixer, the crushing in the Hydro mixer was greater, with more fine grains.

5. Discussion

The comparison of the different aggregate sets show that the Hydro pilot line yields a higher density level compared to RAIN's pilot line for Set1 with RAIN's aggregate. Whereas for Set 2, RAIN's pilot line achieves elevated densities using the Hydro fractions and dry recipe. In comparison with industrial scale, both plants produce densities that can be considered as 'in the normal range'. For Set2 Hydro`s pilot plant is operating very close to its own industrial benchmark. For the Set1 anodes however, the Hydro densities are quite high compared to the industrial anodes whereas RAIN's pilot line yields similar results for both sets. Further work would be needed to determine how different raw materials and processing parameters are influencing this. In addition, a difference in trending for SER and YM, especially at lower binder levels, can be recognized.

5.1. Is this Anode Round Robin a Solid Comparison?

The study followed the principle of single-anode-produced-and-analyzed-per-setting. This is a risk since outliers may not be discovered. However, for both pilot lines, the very even trending across binder levels made detecting any outliers easy; there were a few in the results for Hydro, and some repeats were produced and averaged in. Since trending is important, the 4-anode Set1 study is better and easier to read than the 3-anode Set2 study. If time and capacity allow, the strength of comparisons will always be better when repeats are made.

5.2. Mixing Process Difference

The different production factors in these comparative studies are in the mixing and type of forming. Mixing is discussed here and forming in the next paragraph.
The crushing of the aggregate happens during mixing as shown in Table 11. It was seen that for coarse grains the two mixers had a comparable effect, but the Hydro mixer made more finer grains through the crushing than the RAIN mixer.

Hydro Aluminium uses a mixer rotor that presses the paste down and creates strong hydraulic, squeezing type shear forces against the pan bottom. RAIN uses a rotor in a lift-up mode. Both mixers will case impact crushing during the mixing; Hydro mixes with a tip speed 9.0 m/s for 3.0 minute; and RAIN mixes with a tip speed 12.0 m/s for 10.0 minutes. If impact crushing was the major effect, then the RAIN green paste would give a finer aggregate from extraction analysis than Hydro. The opposite is seen, which means the hydraulic, squeezing type mixing in the Hydro mixer has a significant effect.

5.3. Forming Process Difference

Both forming parameters and forming method have a significant impact on the final anode properties. (Vacuum) vibroforming and hydraulic pressing require different forming temperatures (~160°C vs. ~130°C for the BX112M binder in Set1). Together with the different diving forces of the compaction (vibration and pressure vs. just pressure) it is very likely to cause a different behavior regarding re-arrangement of particles during forming, especially with regards to binder level. In both sets of fractions, it can be seen that the shape of SER (Figure 2, Figure 6) and YM (Figure 4, Figure 8) curves, are quite different comparing the RAIN and the Hydro line.

Whereas the SER curve shape for the RAIN line is steep at low binder levels and trending down, the trend for the Hydro line is much smoother. Both curves draw near each other for increasing binder levels but still maintain a difference of around 2 μΩm at 14.5 wt% and 15.0 wt% (Set1) binder level. A corresponding trend was seen for YM, but going from lower to higher levels. These observations agree with literature on pilot anode production using a hydraulic press. [4]

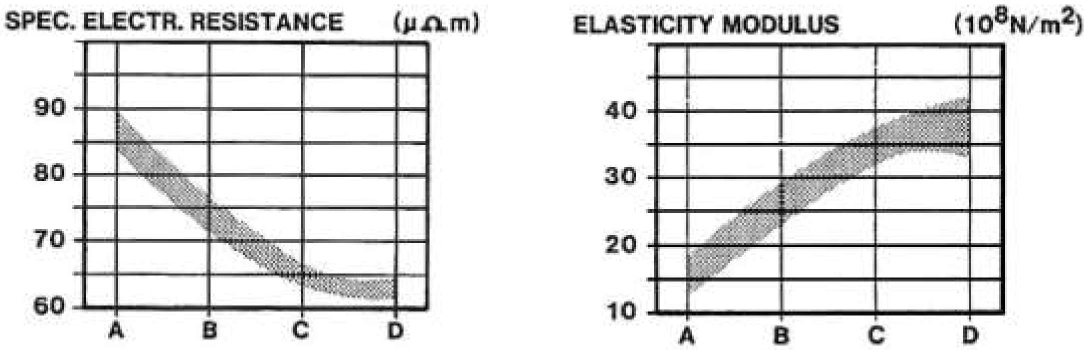

Figure 10. From reference [4], expected trend of Specific Electrical Resistance (SER) and Young's Modulus (YM) with binder level in anodes formed using a hydraulic press.

6. Conclusions

Both pilot anode lines investigated in this study have proven to show repeatable trending within the industrial range. Based on this, both pilot anode facilities are suitable for raw material testing and process optimization studies as an alternative to more costly, and time consuming, industrial trials.

Both pilot anode lines showed significant crushing of the coke aggregate during paste mixing despite different rotor configurations. The push-down method used in the Hydro lab is believed to result in higher compressive shear forces and generation of finer grains. It is not clear how much this influences final anode properties, but the extent of coke attrition is similar to that found in trials with large industrial mixers including co-kneaders.

Operated production equipment and development of operational practices result in good repeatability and meaningful trending at both sites being part of this study.

The analysis round robin indicated some minor issues with the reproducibility of some analysis results, and this will be investigated in more detailed future work.

So far, two comparative studies have been run as part of the technical cooperation between RAIN and Hydro, and exchange of results and discussions have been useful for both parties involved. Similar studies of new material will be arranged.

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