AA14 - The Role of the Alumina Refinery Laboratory: Monitoring, Optimisation and Control of the Bayer Process

Abdulmalik Shaheen[1], Ahmed Ibrahim[2], Abdullah Otaibi[3] and Peter Swash[4]
1. Mine & Refinery Laboratory Superintendent,
2. Engineer,
3. Technical Manager
4. Chief Chemist
Ma'aden Mine & Refinery - Technical Department
P.O. Box: 11342, Al-Jubail Industrial City 31961
Ras Al-Khair Industrial City, KSA
Corresponding author: petermswash@yahoo.com

Abstract

This paper reviews the role of the laboratory in an Alumina Refinery. The key function of the laboratory is in the monitoring of process streams to ensure production is maintained and is essential for quality control purposes. Analytical data on the process streams are constantly fed into a process control system which then automatically makes decisions on the optimal flow conditions in the refinery. During the circulation of liquor throughout the refinery it is imperative to have a constant quantitative understanding of each individual process unit. The equipment used, and the wide variety of routine and non-routine tasks that are conducted are examined. The laboratory also acts in a service capacity to solve a wide range of operational problems, helping reduce operating costs, and improving the overall efficiency of the refinery. Small incremental improvements in a large alumina operation can deliver significant financial benefits when measured over a year. Selected examples of the laboratory's contributions are briefly described. The importance of routine examination of flow streams is critical and helps guide planned and preventive maintenance. Monitoring short and long-term chemical trends in liquor streams can help identify existing and long-term process related issues.

Keywords: Ma'aden, laboratory, quality, Metrohm, alumina.

1. Introduction

It is the quality and production cost of the final product that will determines the success of any alumina refinery. The target is a high-quality alumina product made at a cost lower than its competitors. For this reason, the alumina laboratory provides an important service and support role in process control and monitoring and helps deliver a pure product to the customer.

Simplistically the Bayer process solubilizes alumina from a bauxite, then an alumina-rich liquor is separated from the inert solids. Alumina is then concentrated from the liquor by a seeding procedure. The whole process can be summarized in a simple equilibrium reaction. The forward reaction represents alumina dissolution, and the backward reaction represents seeded precipitation and the regeneration of NaOH.

$$\underset{\xleftarrow[\text{Precipitation}]{\qquad\qquad\qquad\qquad}}{\overset{\xrightarrow{\text{Digestion}}}{Al_2O_3 + 2\ NaOH \rightarrow 2\ NaAlO_2 + H_2O}}$$

In a modern Refinery this chemical reaction is scaled-up and engineered to a size that usually delivers at least 3000 to 6000 tonnes of alumina per day. To deliver a profit the refinery is operated continuously with minimal downtime and operated to deliver the design tonnage. On-line measurements alone are not sufficient for operational purposes and the laboratory must provide other essential analyses to complement the on-line process data. The laboratory also acts as a support and back-up for calibrating and checking the on-line instruments which can malfunction and give misleading results through scaling, corrosion or abrasion. Chemical data on process streams allows calculations to be made on digestion recoveries, flow rates, mass balances, precipitation yields, etc, and enables the whole operation to be continually adjusted and corrected. Without routine chemical analyses the refinery using the automated process system would fail. The analytical data on process streams is built-up into a historical record of operational performance which can then be used for comparison of trends and for trouble shooting and optimization purposes.

Figure 1 identifies the wide variety of roles that the laboratory provides in collaborating with engineers and customers in cost reduction and quality control. Table 1 reviews some of the technical investigations that the laboratory is routinely involved with.

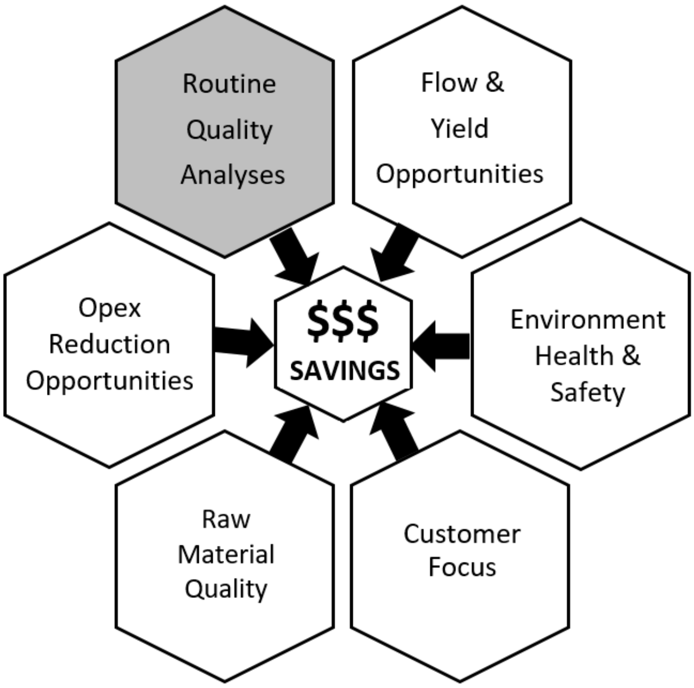

Figure 1. Role of the laboratory for control of operations and in delivering incremental improvements.

Table 1. Main activities within each focus area.

Theme	Activities
Customer Focus	Ensure product (SGA) has the correct specification (particle size, composition, impurities). Supply hydrate particle size and quality, Collaboration, trouble shooting and problem solving, Liaison with smelter laboratories Liaison with reagent suppliers and monitoring lime & caustic quality Liaison with mine and refinery on blending and on operational details. Identifying other uses of products and grow specialty bauxite and alumina uses. Supply MSDS documents, Coordinate sample shipments.

Theme	Activities
Routine Quality Analyses	Deliver quality data on plant samples analysed in a trusted and systematic way Deliver daily routine analyses on samples from around the plant. Laboratory operation - sending quality alerts when analyses are above or below a threshold value, re-sampling and re-analysis. Month end inventory sampling of plant Coordinate sampling of refinery streams, Laboratory auditing.
Flow & Precipitation Yield Opportunities	Providing technical assistance on Bayer chemistry and on optimisation of unit operations and flow streams. Improving and validating existing process models. Support the optimisation and control of process unit operations.
Environmental Health & Safety (EHS)	Advise on safety and environmental issues (air-water-solid compartments). Provide a monitoring role for chemical changes/differences. Hygiene issues. Identifying risks and business opportunities. Characterisation of refinery wastes. Evaluation of waste streams, pollution monitoring.
Opex Reduction - Targeting areas for Improvements	Plant Trouble shooting, participating in de-bottle-necking of plant, Identifying cost-reduction opportunities, conducting audits. Reducing operating costs, and identify capital avoidance opportunities Keeping up with innovation and new developments in chemical analysis, Providing data for cost minimization, continual improvement and identifying cost advantages over competitors.
Raw Material Quality	Monitor caustic and lime quality, Continuous evaluation of reagent efficiency. Test work to help Identify cheaper reagent alternatives. Conducting reagent trials and reagent impact testing.

2. Analytical Tools

The most important piece of analytical equipment in an alumina laboratory is the auto titrator (Metrohm) which delivers a range of analyses on Bayer liquor compositions. These include: g/L Alumina (A), g/L Total Caustic (TC) and g/L Total Alkalinity (TA) (Figure 2). Such parameters are key to understanding and controlling the circulation and movement of the 180,000 tonnes of liquor within the Ma'aden circuit. The analyses allow the characteristics of the liquor to be understood and the daily performance of the Bayer plant to be determined. The FFT (Fluoride Free Titration) method [1] is currently used in preference to the older Watts and Utley method [2, 3, 4]. The equipment is capable of rapid analysis and the data it generates is immediately loaded and delivered to the automatic computer control system. At the Ma'aden Refinery 4 of these machines are set-up for continuous use and are available 24 hours per day. Routine calibration and continuous operation give laboratory and plant personnel complete confidence on the quality of the delivered data. Other analytical tools (Table 2) are also used daily and together supply the main analytical needs of the refinery.

When analyses are above or below a critical threshold value a "Quality Alert" email message is sent to the relevant area team at the refinery. Members of the team must respond and explain such anomalies and get the flow stream re-sampled and re-analysed where necessary. A small change could be the start of a more significant and progressive change, hence the importance of identifying and acting on every small event. This simple system guarantees that no major process problems arise during the daily operation.

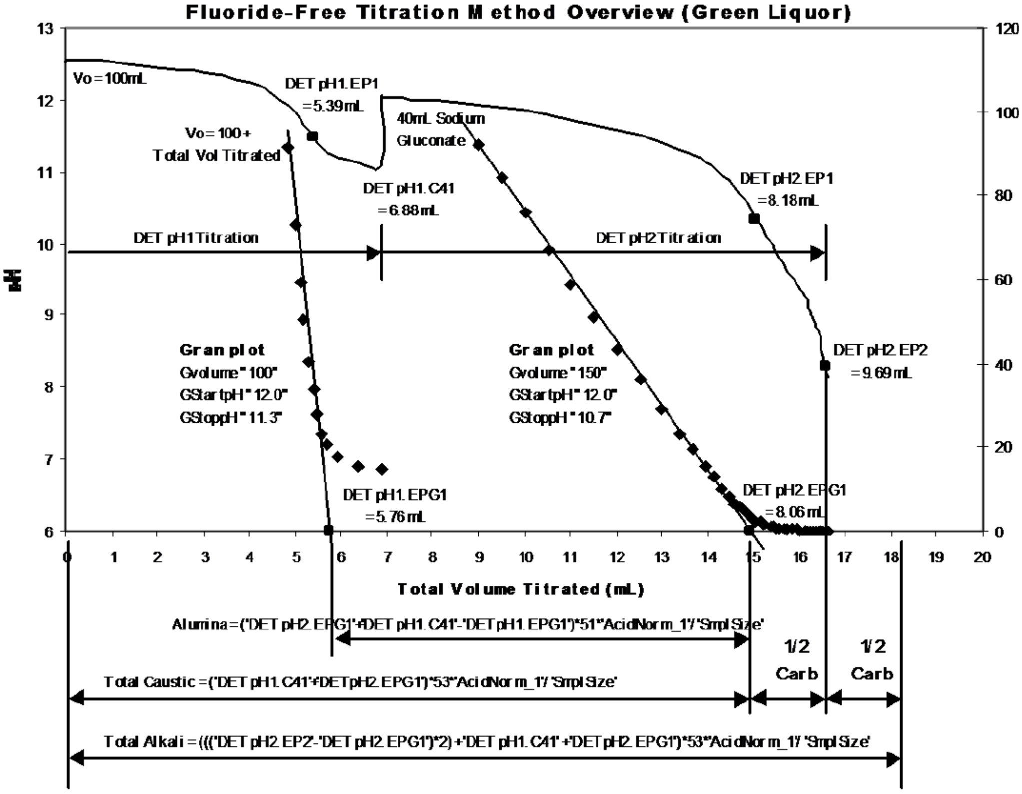

Figure 2. FFT method for the determination of TC, TA and A.

3. Bauxite

The alumina industry typically uses bauxites which are usually well characterized and composed of a limited number of mineralogical components (gibbsite, boehmite, kaolinite, hematite, goethite, quartz, calcite, etc). Liquor compositions are well understood and have well documented physical, chemical and thermodynamic properties [5]. Digestion of bauxites is often predictable and for this reason it is possible to interpret samples using chemical analyses alone. For these reasons expensive pilot plant testing is often not necessary for alumina refinery studies. Small scale laboratory experimental work is still occasionally required and will often focus on areas of uncertainty or process complexity. When the bauxite being processed has typical compositional characteristics a direct comparison can be made with an existing refinery that is processing a similar bauxite. For this reason, confidence on operational performance in many process areas can usually be assured and understood by experienced plant personnel.

Laboratory characterization of bauxites is occasionally needed to identify: bauxite-type, grade and variability. Also, to quantify impurities, and the type and quantity of aluminous phases (boehmite / gibbsite / diaspore). Goethite and hematite contents in bauxite are routinely estimated by using XRD. The crystallinity of goethite may vary from deposit to deposit and this will impact on any XRD quantitative methods. The crystallinity of goethite also appears to increase following digestion.

Mine operations are the favoured place to reduce a range of operational refinery costs by Grade control strategies. This can help control the alumina, silica and iron contents of the bauxite sent to the refinery. The quality of the supplied bauxite tonnage can be improved through detailed chemical analysis and understanding of bauxite profiles from operating pits. This enables a clearer identification of floor and hanging-wall and helps reject quartz, carbonate and kaolinite-rich horizons. The optimum cut-off position in the profile can be identified, which is useful when the silica contact is gradational. Reducing silica in the bauxite supply to the refinery can easily lead to significant saving by reducing the fixed caustic soda losses. However, in Ma'aden a high silica content is needed as the desilication reaction product provides a suitable step for the incorporation and removal of sulphate, carbonate and chloride from the liquor. For this reason, targeting a lower silica content requires modelling to assess the operational and financial benefits.

In bauxite profiles from the Al Baitha Mine an upper iron-rich cap can be identified from visual observation and chemical analyses. In the mill this hard material does not physically break down as fast as the softer friable bauxites. Variable milling characteristics often relate to the quantity of this hard iron-rich bauxite in the mill feed. The hard-cap may constitute less than 25% of the bauxite, but can partially build-up as a critical size within the Mill (<5 cm) and its presence can lead to the recirculation of hard and dense iron material in the hydrocyclone underflow stream.

Table 2. Typical applications of analytical equipment.

Method	Routine Analysis
Auto Titration (Metrohm auto-titrator) (potentiometric acid-base titration).	All Bayer liquor analyses (include filtrates from slurries and decant water). Fluoride free titration method. Lime quality/activity, Al_2O_3 (A), total caustic (TC), total alkalinity (TA), Na_2CO_3 (TA-TC), liquor ratio (A/TC), free caustic determination (FC), raw caustic analysis. Raw caustic impurity determination (e.g. Cl)
XRF (fused bead)	Bauxite (CaO, SO_4 content, impurities), PDS discharge composition (SO_4 content), residue composition, lime impurities, hydrate impurities (Na, Ga, Ca, Fe, P, Si, V, Ti), SGA product impurities (Na, Ga, Ca, Fe, V)
ICP	Liquor Impurities (Fe, Ca, Ga, V, Na, Si, P, Zn, F, S), Bomb digestion liquors (AvA and $RSiO_2$), weak acid leachates (DSP analysis, DSP model development).
Nitogen porosimetry (BET)	Surface area measurement of SGA product Surface area of red mud (allows an assessment of goethite content)
Particle size determination	Laser Sizer - Particle size of TCA and SGA product, >150 µm, <45 µm, <20 µm, flow time, fine sieving
Bomb Digest	Available Na_2SO_4, available NaF, available NaCl, available impurities after digestion, EOC (extractable organic carbon); determination of: - HTAvA %, LTAvA %, $HTRSiO_2$ %, $LTRSiO_2$ %, extractable impurities %, desilication kinetics (0 to 24hrs) at variable water bath temperatures.
XRD	Bauxite mineralogy (goethite, hematite, boehmite, gibbsite content). SGA product (alpha alumina content). Determination of Al content of goethite, scale and precipitate evaluations.
Conductivity	Sea Water (residual Chloride and pH), Condensates
TGA	Bauxite mineralogy (gibbsite / boehmite quantification), LOI (Loss on Ignition), Product (boehmite, moisture quantification), quantification of boehmite, and gibbsite. Quantification of goethite, boehmite and gibbsite in final residue. LOI, moisture of samples, LOI to 400°C (LOI - helps quantify boehmite and gibbsite contents).
TOC / TIC	Organic analysis TOC, EOC / Oxalate (EOC – extractable organic carbon)
Gas Chromatograph	Sodium oxalate determination. Operation of oxalate plant and products. Plant oxalate stability gap point. Critical oxalate concentration.

Method	Routine Analysis
Sieve Screening	Mill Discharge Size (<1.4 mm). Flow test number. Bauxite mill feed size distribution (require large screen 1 to 7.5 cm and larger diameter screens), Verti lime mill discharge psd, simple size-by-size analysis for determining possible bauxite beneficiation options, simulating bauxite washing and bauxite screening operations.
Filtration	g/L solids within slurry samples.
Product Certification	Export/shipping documentation mainly SGA. Supply chemical certificate on important composite samples.
Attrition Testing	Simulates toughness and physical breakdown during calcination or material handling.
Microscopy / Photography	Photographing: - scale, bauxite, filter solids residues physical metallurgy etc for reports and communication. Size analysis and calibration for image analysis software. Monitoring inside of mill, lifter bar wear and ball volumes in mill. Physical metallurgy – initial caustic embrittlement assessment, mill ball quality testing.
Large Water Bath Testing	Settling studies, maintaining temperatures of liquors at 100°C, desilication, liquor holding precipitation reactions, auto-precipitation, reagent testing. Preserving liquor and preventing gibbsite crashing out. Gallium adsorption + elution.
Flowability	Flow funnel testing (function of size and particle shape).

4. Impurities

At Ma'aden the total Iron content of the bauxite is critical to enable the delivery of low iron SGA product. For the Ma'aden refinery a concentration of around 10.6% or more Fe_2O_3 in bauxite is targeted [6]. The relationship between bauxite, plant liquor and SGA are constantly monitored by the laboratory to help guide bauxite blending, to assess the impact of lime slurry addition and to help guide and deliver improvements.

While iron concentrations are measurable in mg/L other impurities are present in g/L, these include sodium sulphate (~2 g/L), sodium chloride (~8 g/L), and sodium carbonate (15 to 25 g/L). Concentrations of these compounds can be partially removed through incorporation into the DSP/Cancrinite framework. Whereas sodium fluoride (~3 g/L) is controlled through incorporation into compounds with a TCA-type composition (e.g. Katoite). Chloride is the most difficult to remove, and for this reason chloride introduction into liquor, mainly as an impurity in the caustic, needs to be minimized. Daily monitoring of impurities is a necessity to identify any significant trends in liquor behavior.

A bauxite DSP factor is used at the Ma'aden refinery to estimate the ability of the bauxite to remove impurities from liquor. This is calculated by using bauxite XRF data and uses available laboratory models on the incorporation of impurities into the DSP lattice [22]. It is simply a guide for bauxite quality and the ability of the refinery to be able to strip CO_3 and SO_4 from the liquor. It is also used as a guide by mine planners to assess bauxite processability and its ability to remove impurities from the liquor. When impurity concentrations in the bauxites are too high or if the silica content is too low, the impurities may build-up in the liquor as impurity inputs will be greater than the outputs. This is mostly relevant to identify possible scaling problems in the Evaporation area if impurities get too high. A basic appreciation of the Le Chatelier's principle, the "common ion effect" and "solubility products" are important in identifying possible precipitation issues and such principles help understand actual precipitation phenomena in the heater tubes. Fluoride compounds have the lowest solubility product and are usually the first compounds to precipitate and scale in the cooler parts of the heater tubes. Such an event is only likely to occur when the Total Soda (TS = TA + impurities) is exceptionally high in the liquor.
Organics and oxalate do not constitute any problems at Ma'aden as concentrations in liquor are very small (oxalate <2 g/L and TOC <4 g/L). Despite the lack of organics in the bauxite the

oxalate gap point test is still carried out to ensure oxalate is sufficiently low. Likewise, the critical oxalate concentration analysis is also routinely carried out. Such monitoring is just to ensure that any trends remain constant and that there are no surprises in the future.

5. Particle Size Distribution

The laboratory is commonly requested to provide particle size distribution data on a range of samples from coarse mill feed (top size ~100 mm) to mill discharge (top size ~2 mm) to SGA (top size ~0.1 mm) to TCA (top size (<0.02 mm). Sieve screening on samples provide data for monitoring purposes, mill models, snapshot surveys and for routine TCA and alumina quality determinations. Size data can simply be compared with normal operational data from the historical database for a simple assessment. When available it can also be compared with samples from other refinery operations to establish operational performance. Laser sizing rather than physical screening is used for the finer particle sizes and is used on TCA and SGA to determine particle sizes down to microns (Table 3). While laser sizing may have its limitations it does consistently delivers repeatable data from the same machine.

A database is ideally required to be build-up over at least 1 or 2 years, using information on feed and exit streams from the individual unit operations. Getting good representative samples is of paramount importance and it is worth sampling on multiple occasions to obtain quality information on its particle size and variability. For larger samples (e.g. mill feed size distribution) historical data is more limited owing to the problems in screening such large samples (typically 200 L drum = ~350 kg).

Upgrading the bauxite quality by screening or washing can be simply simulated in the laboratory by screening a crushed bauxite (top size 2.5cm) using a range of sieve sizes. Usually during bauxite washing simulation the discarding of the finer size fractions (-38 µm) is usually targeted. Size-by-size analysis of crushed bauxite then allows a prediction of alumina and silica grades in the size fractions and allows recoveries and predicted grades to be estimated. Carrying out such an analysis can immediately assess whether bauxite upgrading is worthwhile.

6. Desilication

Experimental laboratory work can simulate desilication conditions and is simply carried out using a hot water bath (95°C) where the samples are continuously agitated (Table 3). Tests for as long as 24 hours are often required to fully assess the achievable rates of desilication. This is important for Ma'aden as SiO_2 can be 7 to 9 % and the coarse kaolinite particles (up to 1mm) desilicate very slowly compared to other bauxites. Calculations on the desilication of the bauxite uses the Na content of the residue to determine the degree of conversion of SiO2 to DSP. For high SiO_2 bauxites these consume a significant amount of caustic and extra caustic addition must be added after desilication to deliver on A/C targets [7]. Factors that affect desilication include: grind size, slurry holding time and temperature, such variables can be easily tested in the laboratory.

7. Digestion and Boiler House

For many commodities piloting of any new operation is an important requirement prior to any plant construction. However, in alumina refining there is a lot of understanding and confidence on the processing of commercially available bauxites which are often processed at numerous other refineries globally (e.g. Weipa. Guinea, Trombetas). Through comparison of chemical data and basic chemical engineering it is possible to predict the bauxite digestion behaviour with confidence. Only when there is a different bauxite quality will there be uncertainty, such is the case with the Saudi Arabian bauxite used in the Ma'aden Refinery. It has ~24 % gibbsite Al_2O_3 and ~24 % boehmite Al_2O_3 and is mined from an ancient laterite deposit (100Ma). In boehmitictype bauxites 99 % of the contained gibbsite will be digested. Boehmite is more difficult to digest but at high temperatures (>250 °C) over 90 % is still be solubilised. For these reasons quantification of boehmite in residue becomes important to assess the digestion losses, which are typically found as coarse undigested particles. TGA, DSC, XRD, ICP, bomb digestion and diagnostic digests can all help in the quantification of the boehmite content ([8] Table 3). In the laboratory using bomb digestions breakpoint digestion studies can be carried using a range of bauxites charges over a targeted A/C range to identify the upper achievable ratio limit.

For high temperature digestion it is a requirement to understand the high temperature mineralogy and the scale that can build-up during digestion. A basic chemical understanding of DSP/cancrinite, TCA, hydrogarnets goethite and hematite under digestion temperatures allows impurity impacts to be easily understood and impurity balance models to be developed. A list of typical compounds identified in high temperature refinery operations is given in Table 3.

The boiler house at the refinery is an essential part of the refinery operation but is often neglected when considering the Bayer circuit. The production of steam is the driving force in achieving the temperature required for efficient bauxite digestion. Condensate is reused in the boiler house, and its quality is important as it can lead to scaling and caustic embrittlement issues. Potable water testing and understanding of the reagents used in boilers are important and routinely analysed in the laboratory. The laboratory analyses boiler samples for conductivity, pH, chloride content, and concentrations of any additives or contaminants in the water.

Table 3. Minerals and chemical compounds found in high temperature alumina refineries.

Mineral / Chemical Composition	
Apatite – $Ca_{10}(PO_4)_6(OH)_6$	Maghemite - Fe_3O_4
Calcium Carbonate Hydroxylapatite	Magnetite - Fe_3O_4
Calcium Aluminium Oxide Carbonate Hydrate	Portlandite - $Ca(OH)_2$
Hydrogarnet - $Ca_3Al_2(SiO_4)_3.y(OH)_{4y}$	Periclase - MgO
Hydrocancrinite – $Na_8(Al_6Si_6O_{24})(OH)_2.2H_2O$	Perovskite – $CaTiO_3$
Hydrocalumite - $Ca_2Al(OH)_6[(OH)_x].3H_2O$	Vaterite - $CaCO_3$
Hydrotalcite - $Mg_6Al_2CO_3\ (OH)_{16}.4H_2O$	Brucite - MgO
Montmorillonite $Na_{0.33}(Al)_2\ (Si_4O_{10})(OH)_2.nH_2O$	Low Ca Cancrinite $Na_2\ [(CO_3)_2|Al_6Si_6O_{24}].2H_2O$
Gibbsite – $Al_2O_3.3H_2O$	Cafetite - $CaAl_2Ti_2O_{12}.4H_2O$
Diaspore - $Al_2O_3.H_2O$	Sodium Aluminium Carbonate
Hematite – Fe_2O_3	Sodium Aluminium Silicate Hydrate
Goethite – $Fe(OH)_3$	Freudenbergite - $Na_2Fe_2Ti_6O_{16}$
Anatase - TiO_2 (leucoxene composition)	$Ca_3[Al,Fe]_2(SiO_4)_n.(OH)_{12-4n}$
Rutile - TiO_2	Hydrogrossularite - TCA
Kassite – $CaTi_2O_4(OH)_2$ (CTH)	Ca-Al-Si Hydroxide - TCAS
Quartz – SiO_2	Kaolinite - $Al_2Si_2O_5(OH)_4$
Katoite - $Ca_3Al_2(SiO_4)_{3-x}(OH)_{4x}$ (x=1.5-3)	Pyrophyllite / Illite / Chamosite
Calcite – $CaCO_3$	Pyrite – FeS_2
Boehmite – $Al_2O_3.H_2O$	Aluminite - $Al_2SO_4(OH)_4.7H_2O$

8. Liquid Solid Separation and Red Mud

In the Settler liquid: solid separation takes place on the blow-off slurry (80 to 90 g/L solids). This is a critical part of the refinery operation. It represents a major bottle neck if separation goes wrong and is a rate determining factor for liquor throughput (Table 4). Most of the liquid: solid tests done in the refinery laboratory are simple settling tests using a standardized settling procedure, carried out in 0.5 L or 1 L measuring cylinders. For testing this is carried out on readily available fresh hot slurry direct from the plant. Generating liquor by bauxite digestion in a large autoclave can be done but does create a significant amount of work and complexity, as it requires the simulation of the actual milling-desilication-digestion-lime addition and flashing conditions within the operating plant.

Changes in bauxite mineralogy can account for variation in settling behavior in settler and washers. Changes can equally be due to changes in stockpile alumina grade which may lead to g/L solids surges, or through variable flocculant behavior under different liquor conditions (e.g. changes in TC/TA). Monitoring g/L slurry solids and bauxite mineralogy (hematite/goethite) can sometimes help explain changes in settler performance after the event and help establish procedures/protocols for any similar future event. Boehmite growth in the flash tanks can increase the g/L solids content in the slurry and impact on settling behavior.

Routine and non-routine analysis of data from the settler and washers allows the plant to be better understood when bauxite quality varies. The operating parameters (e.g. liquor TC/TA, compaction density, settling rate and viscosity of the settled material etc.) can be compared following use of different flocculants and reagent dosages.

Fixed soda consumption is high when SiO_2 content of bauxite is high. Simple calculations allow fixed soda consumptions (per tonne of alumina) to be calculated. The soluble soda component is then typically an extra 5 to 10 % above the fixed soda. The soluble soda content of the mud slurry can obviously be determined more accurately by titration. A further mode of soda is the adsorbed soda component and represents the un-washable soda measured by titration down to 2 gpL Na_2CO_3. The soluble and adsorbed soda is important at Ma'aden as the liquor component that reports to the mud ponds is not recirculated, and any soda lost to this stream will be a financial loss. Hence the need to minimize the caustic loss from the circuit.

As a practice it is suggested that the waste should be washed as thoroughly as possible to ensure that any leachate from the solids does not disperse into ground water. The washing circuit at the Ma'aden alumina refinery ensures a thorough washing of its red mud waste and soluble caustic losses during washing are usually extremely low (<8 g/L).

9. Raw Materials

In collaboration with the procurement department attempts are continuously made to reduce reagent usage and costs, as well as identifying other suppliers who can sell similar products at a lower cost. Costing studies require laboratory testing and evaluation prior to any full-scale plant trials. If a reagent with a totally new chemistry is to be trialed its impact on hydrate precipitation and oxalate precipitation is necessary prior to its full-scale use. Settling and washing operations requires constant engagement with flocculant suppliers to help reduce operating costs and improve settling rates and OF liquor clarity. Laboratory and plant trials are often required on a range of reagents that include: liquor stabilisers, defoamers, dewatering aids, CGM's. Laboratory testing and validation is always required prior to any larger-scale test work. Comparative testing on different reagents and the determination of whether they are cost competitive to existing reagents is an ongoing work activity in the laboratory.

Routinely analyzing the impurity contents of the large tonnage raw materials used in the refinery is necessary as the chloride content of the caustic and the carbonate content of the lime supply can be variable. These are critical elements as such impurities can build-up within a circuit and may not have an immediate exit path from the recirculating refinery liquor.

Table 4. Main unit operations and typical analytical needs and requests.

Operating Area	**Project areas and range of laboratory studies**
Laboratory	Routine and non-routine support to all unit operations. Technical support and model development. Calibration of online instruments, lime characteristics, FEL0 and FEL1 studies, gallium extraction from SL using resins. Impact tests for evaluating additives impact on hydrate precipitation yield & oxalate yield.
Environmental	Dusts and particle sizes. Geomembrane material evaluation, effluents, toxicity of reagents, utilization of bauxite in cements and potential ways to dispose of red mud in cements are also commonly pursued with a utopian dream of their large-scale use. Monitoring Inorganic pollutants in effluents released into the environment. QC on sea water cooling tower discharge.
Modelling	Feed and product analyses for SysCAD, EXCEL, Aspen, JKSimMet models. Evaluating sweetening to improve liquor ratio and lower liquor iron concentrations.
Mining Grade Control and Exploration	Examination of samples, density determination, screen analysis, profile studies, new bauxite evaluations, processability issues, evaluate sweetening bauxites. Vertical and horizontal variability. Evaluate online sampling and analysis possibilities (slurries and solids). FTIR bauxite evaluation (grade control/bauxite samples).
Bauxite Handling and Stockpile	Identification of mine estimations of mined blocks, monitoring analyses of composite train samples, understanding the placing of the individual train loads on selected stockpile for use. Conveyor belt size determination/monitoring. Size calibrations using optical image analysis.
Boiler House	Scale conductivity, cooling water quality.
Crushing, Milling & Hydrocyclones	Drop weight testing, size determinations, mill modelling, sample sizing, mine to mill studies, refining mill model - modelling sampling, hydrocyclone models – density and size predictions, bauxite beneficiation – notably washing.
PreDeSilication (PDS)	Determination rates of desilication based on Na content using tie elements to help define silica conversion. Determination of quartz content of bauxite.
Digestion and Evaporation	Characterisation of scale in JPU and digesters. Simulation of digestion and lime addition operations, digestion modelling, size breakdown shrinking core model, Test on individual size fractions and examination of residue size distributions after digestion, simulation of lime addition, development of impurity balance models (TOC, SO_4, Cl, F, Ga) DSP modelling - dissolution of formed DSP in weak acid or in buffered acetic acid. Guidance on impurity control strategies. Auto precipitation model and quantification, identification of precipitates from different TC liquors, digestion models, energy models, residue characterisation. Breakpoint testing for fluoride precipitation during evaporation. Breakpoint testing for increasing ratio in margin reduction trials
Clarification & Filtration	Settling tests, reagent comparisons, determination of filtration rates Evaluation of over-flocculation (calibration required), to continually evaluate reagent costs and effectiveness, process chemical trials, filter performance, assess blinding of screens, filter solids analysis, particle size of TCA using different lime quality feeds.
Impurity Control	Monitoring of concentrations to identify process risk concentrations, impacts on precipitation yield, TOC destruction, impurity balance model inputs and outputs.
Precipitation	Size determinations, improving aggregation/growth for particles, yield impacts, precipitation model, precipitation shape size nature of hydrate and SGA, looking at sections through grains growth characteristics and incorporation.
Calcination	Breakage, toughness number, SGA comparison with other refineries, attrition.

10. Collaboration and External Research

Bomb digests are now easily carried out in any laboratory especially when microwave digestion equipment is available. This is at least possible for low temperature digestions (150 °C). However, when higher digestion temperatures are required (>250 °C) this is often more of a problem due to the availability of digestion equipment. Equipment must also be immediately available to carry out the liquor analysis. Outside of operating alumina refineries there are only a few commercial laboratories set up to analyse Bayer liquors. Furthermore, when specialized equipment and expertise are not available, use must also be made of autoclaves and larger scale equipment in these laboratories (e.g. CSIRO, Central South University, JNARDDC, Zhengzhou Research Institute). Personnel experienced in aspects of Bayer liquor safety is an important part of working with external laboratories.

The laboratory also provides certified analyses on products and has an important role in examining shipping samples and collaborates closely with smelters who are the customers for the SGA product. Round Robin testing of samples and comparing results with other alumina laboratories is mutually beneficial. Such collaboration with customers and competitors can help standardize methods and calibrate and refine procedures.

The laboratory is a key point of contact for collaboration with local universities as chemists can guide and identify: safe, measurable, achievable, relevant and time-based projects. They also have the expertise to help with sample acquisition, chemical analysis and data interpretation. Fostering collaboration and building local expertise can also help in refinery project execution. A professional openness on environmental and safety related issues is important as well as opening-up the laboratories to school and university visits. Large industries have an important role to play in university research as they can guide graduate and post graduate students towards completing useful and practical projects that have immediate technical significance [9]. The collaboration can also help promote the company as an attractive graduate employer.

11. Alumina Refinery – Human Health Analogy

Figure 3 illustrates some close analogies between the red-end side of the refinery process and human health. The comparison suggests the importance and need of looking after the individual unit operations and monitoring of the circulating fluids. Only through constant sampling and laboratory analysis can the process be fully understood. Otherwise one small problem can cascade through the whole system and lead to reduced operational performance. This comparison illustrates the importance and relevance of a laboratory delivering quality analyses for monitoring purposes and identifying short and long-term problems.

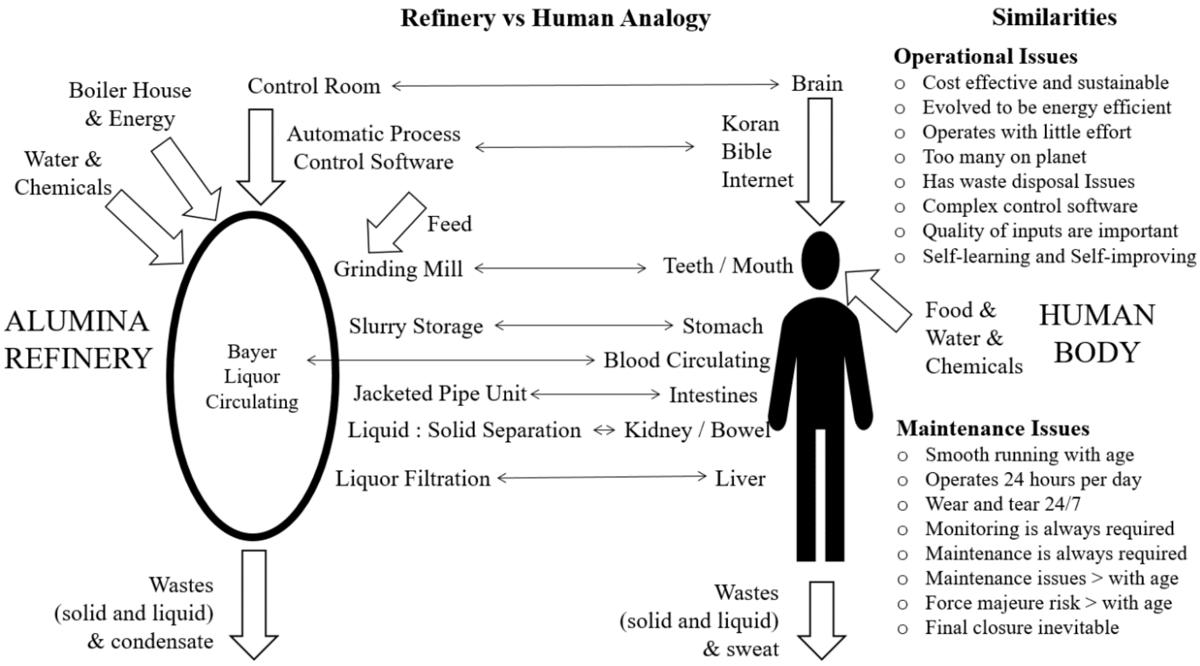

Figure 3. Constant monitoring of health helps guides preventative maintenance.

12. Conclusions

A modern alumina refinery requires a laboratory to supply it with analytical data on a wide range of process streams. The data allows monitoring, optimization, control and adjustment of the process plant. The laboratory has the capability to ensure and certify the quality parameters for the mine and alumina refinery. Compositional trends must be fully understood, and operational changes selected. The idea of process streams being perfectly constant in composition is not realistic in an operating alumina refinery as small changes in bauxite quality can readily take place and the refinery must adapt to these changes which in turn creates further variations throughout the whole plant. Variability may be due to small changes in bauxite: size, hardness, grade, mineralogy or impurity content. These in turn cause changes in liquor composition, fluid flow-rates, settling-rates or in liquor impurity composition over time. For these reasons the laboratory has an influential role to play in analyzing samples and monitoring the chemical trends in the refinery operation.

Focused research projects with engineers and laboratory personnel can contribute towards incremental improvements on the plant. Such improvements deliver important cost savings and help justify laboratory costs and the continual need for the replacement of equipment. Flexibility and the ability to provide data 24 hours a day is the key for a successful laboratory service. The faster the problem can be solved the better for plant availability, liquor flow, precipitation yield, production, and cost savings.

13. References

1. W. Connop, M. Lynton, R. Andrew, Determination of alumina, hydroxide and carbonate in Bayer liquor, *Patent AU1996054698*, filed 1999.
2. S.P. Rosenberg, The Alcoa liquor analyser (ALIAN), *Alumina Quality Workshop*, Perth, 1990.

3. H.L. Watts and D.W. Utley, Sodium gluconate as a complexing agent in the volumetric analysis of aluminum compounds, *Analytical Chemistry*, Vol. 28, no. 11, pp. 1731-1735, November 1956.
4. H.L. Watts and D.W. Utley, Volumetric analysis of sodium aluminate solutions, *Analytical Chemistry*, Vol. 25, no. 6, pp. 864-867, June 1953.
5. E. Königsberger, G. Hefter, and P.M. May, Solubility and related properties in hydrometallurgy, *Pure Appl. Chem*. Vol. 81, No. 9, 1537–1545, 2009.
6. A. Al Ibrahim, A. Hommadi, A. Al-Otaibi, P. Swash, Impurities in Bayer Liquor: Learnings from the Ma'aden Alumina Refinery, *Proceedings of 48th International ICSOBA Conference*, Krasnoyarsk, Russia, 16-20 September 2019, Paper AA03, TRAVAUX 48, 161-171.
7. T. Oku and K. Yamada, The Dissolution Rate of Quartz and the Rate of Desilication in the Bayer Liquor. In: Donaldson D., Raahauge B.E. (Eds), *Essential Readings in Light Metals*, Springer, Cham. 2016.
8. W.E. Wahnsiedler, The Kinetics of Bauxite Digestion in the Bayer Process, *Light Metals* 1985, TMS, Warrendale, 145–182.
9. The Alumina Technology Road Map. Jan 15, 2013 - Alumina. Technology. Roadmap. International Aluminium Institute. Bauxite and Alumina Committee. 2010 Update http://www.world-aluminium.org/media/filer_public/2013/01/15/fl0000422.pdf.