BAUXITE RESIDUE CO_2 MINERAL SEQUESTRATION ASSESSMENT

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ABSTRACT

Since the start of the century, bauxite residue has received re-occurring attention as a potential material for carbon capture and storage. While several studies have explored this possibility, a comprehensive evaluation of the underlying chemistry, technical implications and economic viability for the alumina industry has been lacking. This paper, commissioned by the International Aluminium Institute, addresses these aspects, particularly in the context of securing carbon credits to offset emissions penalties. A typical bauxite residue mineralises approximately 12 kg CO_2 per tonne of dry bauxite residue solids (BR), equating to about 1.5% of an alumina refinery's carbon footprint. A review of the chemistry of CO_2 capture and CO_2 mineral sequestration shows that typically two-thirds of the CO_2 initially absorbed is not mineralised and cannot be mineralised economically, creating a two-fold problem for alumina refiners. Firstly, two-thirds of the flue gas compression energy is wasted and secondly, the heavily carbonated residue liquor cannot be returned to the Bayer process untreated. The Scope 2 CO_2 emissions associated with compression energy consume a substantial fraction of the amount of CO_2 mineralised. Even without considering Scope 2 emissions, both the operating cost and the capital cost would be prohibitive on their own at the commonly used carbon credit projections at or around 100 USD/t CO_2. A carbon credit value of at least 700 USD/t CO_2 is required for the economics to break even. More viable opportunities exist in carbonating lime waste products separate from the residue. The paper discusses important aspects of the chemistry, such as pH rebound, chemical soda loss recovery potential, release of fluoride from tri-calcium aluminate, and operating preferably under reduced carbonation reactor operating pressure and reduced liquor/solids ratio.

Keywords: Bauxite residue, Carbonation, CO_2 storage, Carbon credits, Economics.

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1. INTRODUCTION

Contacting bauxite residue with CO_2 has been the subject of various studies over the past few decades. In some cases, and in two PhD studies, the primary objective was assessing the potential contribution to the effort of reducing global warming [1–3]. In other studies, this was a secondary objective with the main focus being e.g. residue neutralisation [4], more efficient revegetation [5], chemical soda loss recovery [6] or metals recovery [7]. Alcoa had operated a bauxite residue carbonation unit on an industrial scale at Kwinana from 2008 for a few years using CO_2 rich waste gas from a nearby ammonia plant [8]. This was done to improve residue disposal management, while recognising the benefit of reducing the carbon impact of the operation on the climate.

It is widely recognised that bauxite residue can capture and mineralise CO_2. However, the studies published so far present only a fragmented picture. No conclusions have been drawn yet if bauxite residue carbonation is a viable proposition. The alumina industry has embarked on a program of decarbonisation initiatives. It is of interest to the industry to know the impact of bauxite residue carbonation within the overall scheme of initiatives and if indeed bauxite residue carbonation is economically feasible in the first place. The International Aluminium Institute (IAI) commissioned a study to provide answers to these questions; this paper summarises the main conclusions from this study.

Understanding the carbonation chemistry is of crucial importance, as it is the basis for establishing (a) the quantity of CO_2 being captured, (b) the quantity of CO_2 being mineralised, (c) the key carbonation process design criteria and (d) any potential effects there may be on the Bayer process. These factors ultimately determine the cost incurred per net tonne of CO_2 mineralised, being the difference between the amount of CO_2 permanently stored in the residue and the amount of CO_2 emitted to the atmosphere due to the effort to accomplish this. The potential economic rewards are the carbon credits obtained.

2. CARBON CREDITS

Carbon credits can only be claimed when certain conditions are met according to the certification requirements in the applicable country. Carbon credits trading has been established in many economies around the globe, although structure and implementation is not uniform. Schemes vary between being voluntary and being compliance-based. The schemes in the EU and in Australia are compliance-based and are amongst the most developed schemes in the world. Furthermore, with the EU and Australia having well established alumina production facilities, the focus on certification requirements has been directed to those regions in the present study.

In the EU, legislation exists for geological storage of CO_2 but this concerns underground storage [11]. Legislation is under development for ground level storage, but the proposals so far are focused on agricultural and forestry projects and do not include storage in mine waste [12]. Australia is one step further since new legislation appears to apply also to ground level storage in mine waste streams [13]. The legislation distinguishes between 100-year and 25-year permanence projects. In the present study, the projected value of these carbon credits is assumed to be 100 USD/t CO_2.

Common to the EU and Australian regulations are some strict criteria for carbon storage certification. In the EU, these criteria are known as the "QU.A.L.ITY" criteria [14]:

1. QU: QUanitification
Carbon removal activities need to deliver unambiguous benefits for the climate and be measured, monitored and reported accurately. Note that monitoring means monitoring for leakage and that this also needs to continue for a long time after storage closure.
2. A: Additionality
Carbon removal activities need to go beyond existing practices and what is required by law. Note that this implies that any naturally occurring carbonation is excluded and needs be deducted from actively achieved carbonation.
3. L: Long-term Storage
Certificates are linked to the duration of carbon storage and should ensure long-term storage.
4. ITY: SustainabilITY
Carbon removal activities must contribute to sustainability objectives such as climate change adaption, circular economy, water and marine resources and biodiversity.

These criteria imply that certification requires ongoing monitoring and registration of the quantities of CO_2 being mineralised and being maintained in storage. This requires periodic borehole sampling and analysis of the residue deposit area for establishing a baseline and for quantifying any losses over time.

It is noted that there is little published plant information about the extent of passive mineralisation of CO_2 in bauxite residue, except for XRD results of material from a 14-year old residue deposit in Texas which still showed considerable presence of TCA (active calcium compound, see under 3.1.4) in the top 15 cm layer and no change in TCA and calcite profiles below a depth of 60 cm [5]. This suggests that the CO_2 mineralisation rate in residue deposits under atmospheric CO_2 pressure is extremely slow and the overall CO_2 mineralisation is probably close to being negligible.

3. CHEMISTRY OF CO_2 MINERAL SEQUESTRATION

The chemistry of CO_2 mineral sequestration involves two steps:
1. Carbon capture: CO_2 capture from a waste gas or from the atmosphere;
2. Carbon mineralisation: Binding the captured CO_2 in the form of a solid compound.

Step 2 must lead to a long-lasting compound or compounds in order to deliver benefits to the climate and satisfy carbon credits certification. One such compound is calcite, $CaCO_3$, at least when present in a long-lasting alkaline environment, thus not in contact with an acidic soil cap.

3.1 CO_2 Capture

The dissolution of CO_2 in Bayer liquor involves reaction of the acidic CO_2 with the alkaline compounds of the liquor, whereby the pH reduces. The hydroxyl (OH^-) ions and aluminate ($Al(OH)_4^-$) ions are two of the main alkaline species. Below a pH of about 10–11, the aluminate ions substantially dissociate into chiefly an $Al(OH)_3$ precipitate and OH^- ions. The other main alkaline species is carbonate CO_3^{2-}. The alkaline anions are charge balanced by cations. In Bayer liquor the cations are predominantly sodium ions, Na^+, and in water hydrogen ions, H^+, often referred to as protons. Dissolved CO_2 in an aqueous solution is in equilibrium with H_2CO_3, which behaves as an acid since it is a proton donor. CO_3^{2-}, present in Bayer liquor, behaves as a base since it is a proton acceptor. Their acid-base reaction produces bicarbonate (HCO_3^-), which is amphoteric, because it can either accept or donate protons.

The dissolution of CO_2 correlates with a number of equilibrium type reactions that involve:

- gaseous $CO_2(g)$
- dissolved CO_2
- neutral carbonic acid H_2CO_3
- monovalent bicarbonate HCO_3^-
- divalent carbonate CO_3^{2-}

These reactions and their equilibrium correlations are described in e.g. Plummer and Busenberg [15], which has been the source of the equilibrium constants presented hereafter. Their correlations provided the basis for developing the corresponding graphs in Figures 1–4.

Since bauxite residues at the final point of refinery discharge are usually in the temperature range of 50–60 °C and flue gasses will not likely be available at temperatures below 60 °C, the thermodynamic data hereafter is presented at 60 °C. Another reason for choosing this temperature is reaction kinetics. The optimum temperature for the carbonation rate of bauxite residues and other alkaline waste materials was found to be in the range of 50–60 °C [9,10]. Although the solubility of CO_2 in aqueous solutions reduces with increasing temperature, just as for other gases, the solubility of the desired calcite precipitate also reduces. In combination with the temperature effect in the Arrhenius term of the rate equation, temperatures in the indicated range appear to provide the highest calcite precipitation rate, thus highest CO_2 mineralisation rate.

The CO_2 concentration in the gas phase, thus the CO_2partial pressure (strictly speaking the CO_2 fugacity) determines the concentration of $CO_2(aq)$ in aqueous solution through Henry's law:

$$\begin{aligned} CO_2(g) \leftrightarrows CO_2(aq) : K_h = [CO_2(aq)] \,/\, P_{co2} \quad &= 0.00016 \text{ mol/(L.kPa) at } 60\,°C \\ &= 0.00034 \text{ mol/(L.kPa) at } 25\,°C \end{aligned} \qquad (1)$$

The $CO_2(aq)$ is present in two forms which are difficult to distinguish analytically: CO_2 and H_2CO_3. Therefore, they are commonly combined and given either the term $CO_2(aq)$ or H_2CO_3, thus $[CO2(aq)] = [H_2CO_3] = [H_2CO_3]_{used} = [CO2] + [H_2CO_3]_{actual}$.

$$CO_2 + H_2O \leftrightarrows H_2CO_3\text{actual} : Ko = [H_2CO_3]\text{actual} \,/\, [CO_2] = 0.0017 \text{ mol/L at } 25\,°C \qquad (2)$$

This indicates that $[H_2CO_3]_{actual}$ is less than 0.2% of $[H_2CO_3]_{used}$. Equilibrium (2) is normally not applied, since in expression (1) and expression (3) hereafter either $CO_2(aq)$ or $[H_2CO_3]$ is used.

$$H_2CO_3 \leftrightarrows HCO_3^- + H^+ : K_1 = \alpha_1 [HCO_3^-] \cdot \alpha_1 [H^+] \,/\, [H_2CO_3] = 5.13E\text{-}07 \text{ at } 60\,°C \qquad (3)$$

$$HCO_3^- \leftrightarrows CO^{2-} + H^+ : K_2 = \alpha_2 [CO_3^{2-}] \cdot \alpha_1 [H^+] \,/\, \alpha_1 [HCO_3^-] = 7.18E\text{-}11 \text{ at } 60\,°C \qquad (4)$$

$$H_2O \leftrightarrows OH^- + H^+ : K_w = \alpha_1[OH^-] \cdot \alpha_1[H^+] = 9.55E\text{-}14 \text{ at } 60\,°C \qquad (5)$$

By increasing the CO_2 partial pressure, the H_2CO_3 concentration increases because of reactions (1) and (2) and, consequently, reactions (3) and (4) tend to shift to the right. That happens indeed as far as the H^+ concentration is concerned, thus the pH reduces. The H^+ concentration in the equilibrium constants K_1 and K_2 is that of the reactions (3) and (4) combined. Hence $[H_2CO_3]/ [HCO_3^-]$ and $[HCO_3^-]/[CO_3^{2-}]$ increase to maintain the equilibrium values of K_1 and K_2. Le Chatelier's law of resistance to change is obeyed. The increase in H^+ concentration is resisted by producing more HCO_3^- and H_2CO_3. Thus reactions (3) and (4) are shifted to the left by the disproportionate increase of the H^+ concentration. This hydrogenation of carbonate, being the opposite of the energy intensive breaking up of the hydrogen carbon bond, is an exothermic reaction. So-called Bjerrum plots depict the relative concentrations of the carbonate species as a function of pH.
Examples are shown in Figure 1.

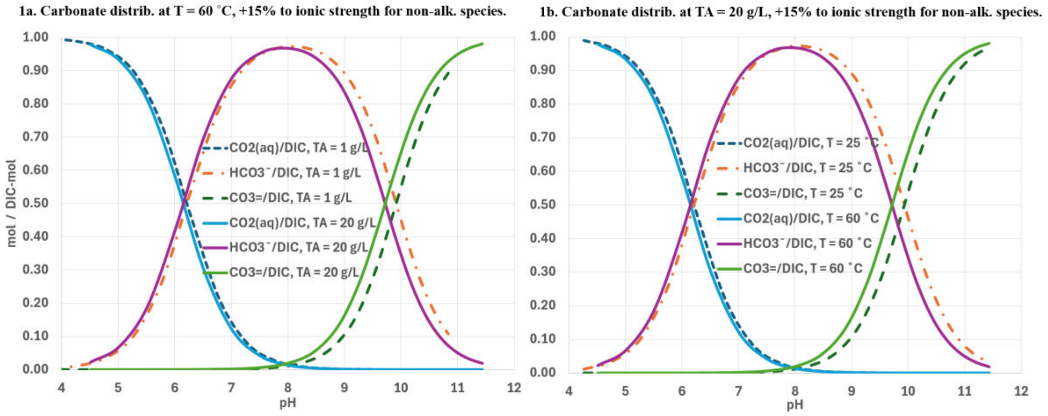

Figure 1. Bjerrum plots for carbonated bauxite residue liquor. Left: a) Sensitivity to TA (= S or TTS) expressed as g/L Na_2CO_3, Right: b) Sensitivity to temperature.

3.1.1 Role of Soda Concentration

The effect of CO_2 partial pressure on the amount of CO_2 absorbed and on the pH in Bayer liquor is dependent on the sodium concentration $[Na^+]$ associated with alkalinity. In American Bayer terminology this term is known as TA (Total Alkalinity) or TTS (Total Titratable Soda) or S concentration, with all terms usually expressed as equivalent g/L Na_2CO_3. The term TA is used hereafter. When Na^+ ions are present they complement H^+ in charge-balancing CO_3^{2-} and HCO_3^- thereby allowing more CO_2 to be absorbed. The CO_2 absorbed is often expressed as dissolved inorganic carbon (DIC), being:

$$DIC = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3], \text{ expressed in equivalent g/L } CO_2 \qquad (6)$$

If the activity coefficients were all equal then a change in $[Na^+]$, hence a change in TA, would not alter the profiles of relative species concentrations as a function of pH as depicted in Bjerrum plots. However, the activity coefficient of CO_3^{2-}, being a divalent ion, is smaller than that of the other ions present, being monovalent, hence its thermodynamically apparent concentration compared to its actual concentration is lower than for the other ions involved in the above reactions. This disparity increases with increasing concentration, thus with increasing TA. On the other hand, $CO_2(aq)$ has no charge, thus its apparent concentration is approximately equal to its actual concentration. This makes the species profiles as a function of pH being compressed like a spring to the left when TA is increased, see Figure 1a. Increasing the temperature results also in a shift of the profiles to the left, since the system tries to resist the exothermal effect of the binding of hydrogen to carbonate, again by Le Chatelier's principle, see Figure 1b. The activity coefficients in these plots have been calculated using Davies' equation, which provides a good approximation of activity coefficients for ionic strengths below 0.5 mol/L applicable to the residue carbonation conditions of interest [16]. The ionic strengths of the liquors have been assumed to be 15% greater than calculated on the basis of just the alkalinity related anions and cations to account for the non-alkaline liquor impurities. Note that the concentration of non- alkaline divalent ions, such as sulfate, have a disproportionate high impact on the ionic strength.

The quantity of CO_2 absorbed over a given pH interval during residue carbonation is proportional to TA, just as is applicable to a titration quantity in determining TA in the laboratory, see Figure 2a. Reducing the pH over that given pH interval requires less neutralisation for a low value of TA than for a high value of TA, thus requires a smaller CO_2 partial pressure increase, see Figure 3. The resulting DIC as a function of CO_2 partial pressure for different values of TA is shown in Figure 2b. Note in Figure 2a the relatively small change in DIC over the pH interval of roughly 8.5 to 7.5 corresponding with the top of the HCO_3^- bell curves in Figure 1.

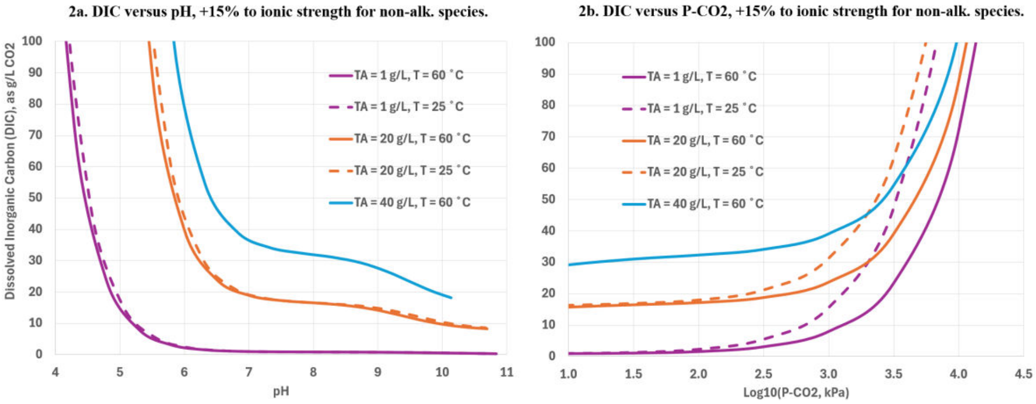

Figure 2. Dissolved inorganic carbon in carbonated bauxite residue liquor. Left: a) as a function of pH, Right: b) as a function of CO_2 partial pressure.

It can be concluded that the quantity of CO_2 absorbed increases when the CO_2 partial pressure is increased and when the TA is increased. Furthermore, at a low TA the pH drops much further for a given CO_2 partial pressure increase than at a high TA, see Figure 3.

3.1.2 pH Rebound

The above reactions are equilibrium reactions, thus reversible reactions. If the CO_2 partial pressure is reduced, e.g. by exposing the liquor to the atmosphere (p_{CO_2} = 0.043 kPa), then $CO_2(g)$ will be released to the atmosphere through the conversion of bicarbonate to carbonate following Henry's law, and the pH will rise to about 9.5 – 10.5, depending on the TA of the liquor (see Figure 3). The only captured CO_2 that remains in the liquor is the carbonate that resulted from the conversion of aluminate and hydroxyl ions. This reverse reaction of bicarbonate to carbonate is known as pH rebound. The loading and unloading of liquor with CO_2 can be repeated infinitely as long as the alkaline anions are not substituted by acidic anions through e.g. addition of sulfuric acid or gypsum ($CaSO_4{\cdot}2H_2O$). Important is the observation that the pH rebound is a very slow process that may take several days [1, 3, 17–20].

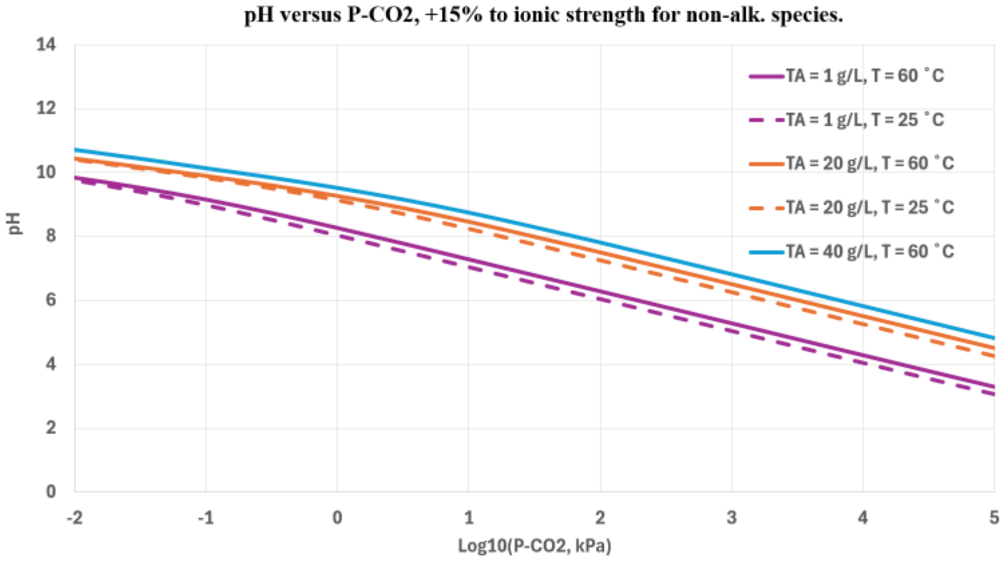

Figure 3. The pH of a carbonated bauxite residue liquor as a function of CO_2 partial pressure.

Apart from the alkalinity in the original liquor, there is alkalinity that enters the liquor through dissolution of species present in the solids when the pH reduces during carbonation. The solids contain alkaline species associated with (a) sodium and (b) calcium. The former is predominantly represented by sodalite, the most commonly found desilication product (DSP) present in most bauxite residues, the latter predominantly by tricalcium aluminate (TCA), a product originating from lime additions to the Bayer process.

3.1.3 Sodalite Contribution

Sodalite ($Na_6(Al_6Si_6O_{24}).mNa_2X.nH_2O$, $0<m<1$, $n<8$) is a zeolite with a basic unit cell structure of a shell enclosing a cage. The cage creates room for enclosure of water molecules and sodium salts. Post digestion the cage is generally almost fully occupied with sodium salts [21]. At this stage, the sodium content in sodalite in Bayer liquor is divided into roughly 75% being in the shell and roughly 25% being in the cage. The shell sodium is interwoven as a charge balancing element within the silica-alumina tetrahedral structure and the cage sodium is associated with said sodium salt anions. The most common of such anions (X in the above formula) are sulfate, chloride, carbonate, aluminate and hydroxyl. The last three anions are the alkaline components of the sodalite. Smith et al. [22] found that on dilution (cold water washing) the aluminate and hydroxyl ions move out of the cage. The cage window is large enough (~2.3 Å) for those ions to pass through but too small for the sulfate and chloride to escape. This is a fortunate circumstance, because generally one would like to recover aluminate and hydroxyl but rather keep sulfate and chloride locked up in the DSP. Although carbonate is also too large to pass through the cage window, it was found that it did manage to escape to a certain extent. It is believed that it managed to do so because of the equilibrium reactions discussed, whereby part of the carbonate is present as CO_2 which is small enough. Smith et al. removed 15% sodium from the DSP through washing.

The data presented in the few papers on bauxite residue carbonation where the sodium concentration in the liquor was also measured, shows that sodium extraction at ambient temperature increased up to about 17% of total Na_2O in the solids by reducing the pH down to pH 7 [3,7]. The driving force here is not dilution but presumably the reduction in OH^- and CO_3^{2-} concentrations (in favour of HCO_3^-) during carbonation, pulling CO_3^{2-}, $Al(OH)_4^-$ and OH^- out of the DSP cage together with Na^+ for charge neutrality. Further studies showed that below pH 7, the sodalite shell starts to break down, especially below pH 6.5 [6,23].

It is interesting to see in test work by Moreno [3] that during the pH rebound, the sodium concentration reduced again, suggesting that the increase in CO_3^{2-} and OH^- concentrations led to a reverse migration of sodium ions and associated alkaline ions back into the sodalite cage. Hence, these exchanges of ions between cage and liquor appear to be also equilibrium reactions to a certain extent. Mass transfer limitations of these ion migrations between bulk liquor and DSP cage, buffer the pH decrease and pH rebound compared to solids free liquor. This is apparent from pH versus time plots in several publications, notably in [1].

3.1.4 TCA Contribution

Calcium aluminates are an important source of alkalinity. Calcium aluminates can be present in various forms e.g. combined with hydrate and silica in various interchangeable proportions, ranging from $3CaO.Al_2O_3.6H_2O$ (known as tri-calcium aluminate (TCA)), being a hydrogrossular to $3CaO.Al_2O_3.3SiO_2$ (known as grossular), with different hydrogrossulars in-between. The metastable precursor form hydrocalumite may also be present [24]. TCA is the most prominent form in the residue and originates from lime usages in the refinery, e.g. as undesired byproduct of causticisation and as deliberately formed TCA filter aid for polishing filtration. Digestion discharge may contain silicated forms of hydrogrossulars, denoted as TCAs and CAs. Hereafter these are included in the term TCA, which represents tri-calcium aluminates in general.

3.2 CO_2 Mineralisation

Kirwan et al. [18] report that TCA buffers at ~pH 11, while titration experiments by Khaitan et al. [25] indicate TCA buffering in the pH range 8.7 to 9.9. This suggests that TCA becomes unstable below pH 11 but its dissolution only significantly starts below pH 10.

$$3\ CaO.Al_2O_3.6H_2O(s) \leftrightarrows 3\ Ca^{2+} + 2\ Al(OH)_4^- + 4\ OH^- \qquad (7)$$

The overall reaction:

$$3\ CaO.Al_2O_3.6H_2O(s) + 3CO_2(g) = 3CaCO_3 + 2Al(OH)_3(s) + 3H_2O \qquad (8)$$

The quantity of CO_2 captured through the alkalinity of TCA equals the quantity of CO_2 that can be mineralised as $CaCO_3$ by the calcium present in the TCA. Thus the TCA alone can do both duties at the same time, at least if the pH is reduced to below 10 to allow the TCA to dissolve. The quantity of CO_2 that is equal to the quantity of CO_2 captured by the alkalinity of the liquor and that of the DSP does not contribute to the formation of $CaCO_3$. This quantity of CO_2 will need to be mineralised without the assistance of TCA, otherwise it will remain in the liquor.

Of note is the role that TCA plays in purging fluoride from Bayer liquor. Fluoride is enclosed into TCA as Al(OH)3F- during the transformation of hydrocalumite to TCA [26]. A build-up of fluoride in plant liquor that also contains sulfate may lead to kogarkoite ($NaF.Na_2SO_4$) precipitation which causes major disruption in hydrate classification and scaling issues in evaporators. Residue carbonation will release the fluoride into the residue liquor. Release of oxalate from calcium oxalate, if disposed of in the residue, is a similar problem.

The other calcium compounds present in the residue generally do not contribute to the mineralisation of captured CO_2. Those other calcium compounds are either already present in the carbonated form, such as the calcium carbonate from causticisation and the calcium carbonate in cancrinite ($Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2{\cdot}2H_2O$), or they are too stable to dissolve, such as perovskite ($CaTiO_3$) present in high temperature digestion residues and carbonate-apatite present in phosphor containing residues in which calcium is partly carbonated anyhow. Residues from karst bauxites found in e.g. Eastern Europe, contain calcium silicates that can be converted under high temperature and pressure to cancrinite [7]. However, the amount of carbonate mineralised this way is insignificant and the conditions too extreme to be considered.

3.2.1 Pressure Limitation and Liquid/Solids Ratio Limitation

Mineralisation as calcium carbonate works best under conditions of low calcium carbonate solubility.

$$CaCO_3(s) \leftrightarrows Ca^{2+} + CO_3^{2-} : K_c = \alpha_2[Ca^{2+}] \cdot \alpha_2[CO_3^{2-}] = 1.74\text{E-}09 \text{ at } 60\ °C\ [15] \qquad (9)$$

It is common knowledge that calcite readily dissolves under acidic conditions. Khaitan et al. reported calcite dissolution below pH 6 in long term titration experiments, causing buffering of the pH between 6.0 and 4.5 [25].

Figure 1 shows that the CO_3^{2-} concentration drastically reduces with decreasing pH. According to equation (9) this leads to an exponential increase of the equilibrium Ca^{2+} concentration, notably below a pH of about 7. Again, there is a dependence on TA, because the carbonate concentration is roughly proportional to TA at constant pH. This effect is depicted in Figure 4a. Since pH is a function of CO_2 partial pressure, as shown in Figure 3, there is a combined effect of CO_2 partial pressure and TA on the equilibrium Ca^{2+} concentration. This is depicted in Figure 4b.

Although maximising the CO_2 partial pressure maximises CO_2 capture, as shown in Figure 2b, it also maximises the equilibrium calcium concentration with calcite in the liquor thereby reducing the CO_2 mineralisation quantity as well as the CO_2 mineralisation rate at the reduced pH values obtained. There is an optimum CO_2 partial pressure for a given TA whereby the conditions for CO_2 mineralisation as calcite are optimum. This optimum pressure corresponds with a pH whereby the dissolution rate of TCA is fast, but the solubility of calcite is still very low. This optimum pressure decreases with reducing TA of the liquor; thus, it is better to use liquors with modestly high TA, e.g. greater than 20 g/L, which one would often obtain anyway after the dissolution of DSP alkalinity. Importantly, a low liquor/solids ratio (L/S) is preferred for maximising the CO_2 mineralisation rate, since DSP alkalinity as well as TCA are dissolved in a smaller volume of liquor, boosting both the liquor TA and the liquor calcium concentration, while reducing the equilibrium calcium concentration with calcite. The latter leaves less calcium unused once equilibrium with calcite is reached. For these reasons, dilution should not be applied. Such measures ensure that the maximum amount of calcium from the TCA converts to calcite and at a maximum rate. Furthermore, operating with a low L/S ratio and not applying dilution also minimise the volume of heavily bicarbonate liquor post carbonation that must be dealt with and it also facilitates refinery water balance control.

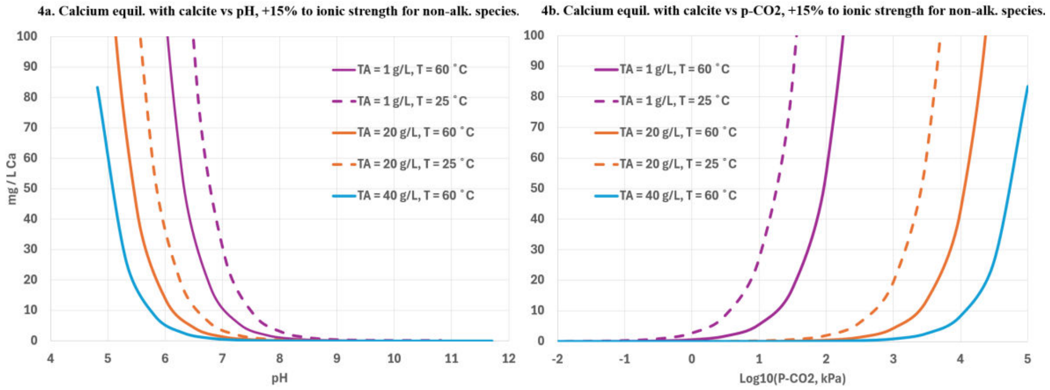

Figure 4. Equilibrium calcium concentration with calcite in carbonated bauxite residue liquor. Left: a) as a function of pH, Right: b) of CO_2 partial pressure.

Experimental results presented in a thesis by Tran [1] (in its table 4.3), whereby the residue composition after carbonation is presented as a function of the CO_2 percentage of a gas applied at atmospheric pressure, show a maximum in the calcite content of the carbonated residue at 30% CO_2 over a range from 15 to 60% CO_2. The residue samples had been diluted by adding 500 mL distilled water to 100 g residue sample. Although the TA was not specified, it is estimated that this would have been about 4 g/L, taking extraction of soda from DSP into account. These data underpin the proposition that an optimal CO_2 partial pressure exists for CO_2 mineral sequestration during residue carbonation. Thus, for mineralising CO_2 as calcite under less desired conditions of a relatively low TA and relatively high L/S, it is important that modest CO_2 partial pressures are applied, sufficient for dissolving all TCA, but not high to the extent that the rise in equilibrium calcium concentration with calcite starts to interfere with CO_2 mineralisation.

3.2.2 Dawsonite

For CO_2 mineralisation as a sodium compound only dawsonite is relevant. Soda ash or simply soda (Na_2CO_3) and sodium bicarbonate, better known as baking soda ($NaHCO_3$), are too soluble, and the latter also too unstable.

Dawsonite ($NaAlCO_3(OH)_2$) is a naturally occurring mineral that has been investigated as a possible feedstock for alumina production [27] and as a possible flame retardant as an alternative to aluminium hydroxide. Dawsonite is also known from the Dawsonite process as a method for purging liquor impurities from a refinery via a bleed stream while recovering the contained soda and alumina values through carbonation to dawsonite and subsequent calcination to sodium aluminate ($NaAlO_2$) [28]. Although some researchers have questioned the stability of dawsonite as a permanent CO_2 sequester, it is likely stable enough for such purpose if stored under the alkaline conditions of a residue disposal area. However, the primary question is: will dawsonite be formed in the first place?

Despite the frequent mention of dawsonite in various papers as a possible residue carbonation product, no research has provided solid proof that dawsonite was formed at more than a trace amount. XRD results presented by Qin [29] show the presence of dawsonite, but the body of the text attribute these peaks to "possibly" corresponding to dawsonite. Similarly, in research published on carbonating mixtures of saline wastewater from oil-fields with bauxite residue to capture CO_2 [31], it is suggested that dawsonite is one of the products formed. However, this conclusion is entirely based on thermodynamics modelling. Kinetic aspects were not considered in the modelling. The researchers were not able to identify all the minerals formed in their testwork, also not dawsonite, because of their amorphous nature.

Thermodynamically, at sufficiently high $[HCO_3^-]$ and $[Na^+]$, dawsonite is more stable than gibbsite and its polymorphs bayerite [32] and nordstrandite [33] in accordance with the following overall reaction:

$$NaAlCO_3(OH)_{2(s)} + H_2O \leftrightarrows Al(OH)_{3(s)} + HCO_3^- + Na^+ \qquad (10)$$

However, dawsonite formation is kinetically disadvantaged by Ostwald's rule that less stable compounds tend to be formed first, especially in the absence of dawsonite seed and more so in the presence of gibbsite and aluminous goethite seeding sites, which are abundantly available in bauxite residue. Below 100 °C gibbsite and/or bayerite are the usual products formed, often from meta-stable pseudo-boehmite as a precursor precipitate, notably for bayerite, especially in residue free liquor. Pseudo-boehmite (γ-$AlOOH.nH_2O$) is a gelatinous boehmite that has water molecules incorporated in the lattice (n roughly between 0.2 and 0.6). Whereas pseudo-boehmite is very unstable, boehmite (γ-$AlOOH$), which is formed above 100 °C, is a very stable compound.

Marinos et al. [30] investigated avoiding dawsonite formation in precipitating aluminium hydroxide from synthetic Pederson process leach liquors, which are comparable with Bayer liquors, at 40 °C through carbonation with CO_2 gas for 70 minutes. TA values of the liquors ranged from 61 to 201 g/L expressed as Na_2CO_3 of which a constant 41 g/L was present as TC ($NaOH + NaAl(OH)_4$) and the rest as genuine Na_2CO_3. The A/TC was 0.40. At a TA of 61 g/L predominantly pseudo-boehmite was formed, at TA of 81 to 101 g/L bayerite was the significant phase and at 121 g/L and higher dawsonite. The rate of pH drop at 61 g/L TA would have been faster than at 201 g/L TA at the constant CO_2 partial pressure applied (see Figure 3). One possible explanation of the observations is that a relatively fast drop in pH, such as at 61 g/L TA, evokes a relatively high alumina supersaturation resulting in primary nucleation of pseudo-boehmite, which subsequently transforms into bayerite, or nucleation and precipitation of bayerite directly at a slightly lower supersaturation. A very low pH reduction rate would allow dawsonite to be formed directly. Also aging of the thus obtained precipitate at 61 g/L TA within the reactor vessel resulted in transformation of pseudo-boehmite to bayerite and subsequently to dawsonite, in accordance with Ostwald's rule. These results demonstrate that even in a residue free liquor of relatively low TA it is not straightforward to produce dawsonite unless low CO_2 absorption rates and/or long aging periods are applied.

In the 1940s the lack of availability of low silica bauxites in some regions, especially the USA, a sintering process utilising soda and high silica bauxite was used by some refineries, this produced sodium aluminate and CO_2 [34]. This was known as the Deville-Pechiney process [35]. After sodium aluminate dissolution, $Al(OH)_3$ was precipitated by cooling and passing through the CO_2 that was generated in the sintering step. Soda was recovered through evaporation and then recycled to the sintering step. A similar process using limestone ($CaCO_3$) is still being used in Russia and China to produce alumina from silica rich ores. Here, $Al(OH)_3$ is also partially precipitated by introducing CO_2 [36]. Carbonating Bayer liquor with CO_2 gas was also widely used to make sub-micron aluminium hydroxide for use as a flame retardant and paper filler. It shows that commonly $Al(OH)_3$ is precipitated when a Bayer liquor is contacted with CO_2, especially when some $Al(OH)_3$ seed is already present.

In a 2011 patent filed by Worsley Alumina [37] regarding a method of carbon capture and sequestration using waste TCA products, a process step is described in which a washer overflow liquor is carbonated with a CO_2 containing flue gas. This results in the precipitation of $Al(OH)_3$, which is then separated from the liquor that continues to a next process step in which TCA is mixed in with the liquor. Also, here, there is no mention of dawsonite formation.

Further evidence that dawsonite is not formed, at least not to any noteworthy extent, can be deducted indirectly from some post carbonation liquor results presented in two papers [3, 7]. They show elevated Na^+ extractions into liquor to an extent that makes it unlikely that any Na^+ extracted would have reacted to $NaAlCO_3(OH)_2$. All $Al(OH)_4^-$ had disappeared from the liquor, including any of the $Al(OH)_4^-$ that was extracted together with Na^+ from DSP. The Na^+ stayed in the liquor and the $Al(OH)_4^-$ vanished. Furthermore, the concentration of carbonate had doubled and reduced again after prolonged exposure to atmosphere. These observations do not agree with a postulation that dawsonite is being formed during these bauxite residue carbonation experiments.

It is concluded that if any dawsonite is formed at all during residue carbonation it would only be to an insignificant amount. Therefore, dawsonite is discounted as CO_2 mineral sequester.

3.2.3 Addition of Calcium from an External Source

Sodium cannot contribute as a cation in CO_2 mineral sequestration. Only calcium can, and the only calcium source in the residue available for this purpose is TCA. However, the amount of CO_2 mineralised equals the amount of CO_2 that the alkalinity of TCA has captured. The only additional way of mineralising the CO_2 captured by the liquor alkalinity and DSP alkalinity is adding a foreign supply of alkali-earth metal ions, such as calcium or magnesium. Both these metals are present as cations in seawater and in waste brine from oil winning.

Seawater is being used for bauxite residue neutralisation at some refineries. A pH of approximately 8.5 can be achieved. As it is rich in Ca^{2+} and Mg^{2+}, seawater neutralisation produces insoluble species such as hydrotalcite ($Mg_5Al_2(CO_3)(OH)_{16}\cdot4H_2O$), brucite ($Mg_3(OH)_6$), calcite ($CaCO_3$), magnesite ($MgCO_3$) and dolomite ($CaMg(CO_3)_2$) [18, 23]. Neutralisation with seawater shifts the alkalinity of the bauxite residue from a strong base associated with sodium ions to a weaker base nature associated with calcium and magnesium ions. The overall alkalinity (hence CO_2 capturing potential) is not affected. There is not much mention in the public domain about using seawater for mineralising CO_2 captured by bauxite residue. Residue carbonation is seen as an alternative option for residue neutralisation, thus for replacing seawater neutralisation rather than complementing seawater neutralisation to achieve simultaneous CO_2 sequestration. If proven to be feasible as such it would only be suitable for refineries with access to seawater and be dependent on environmental licensing. Certification for carbon credits is questionable in view of the criteria discussed in the foregoing.

There was some research done using BAUXSOL™, which is a trademarked product from bauxite residue according to a process that includes neutralisation with seawater or with concentrated brines [38]. This testwork was done in conjunction with tests using regular bauxite residue. It concerns a preliminary study. The regular bauxite residue as well as the BAUXSOL™ were diluted with distilled water by a factor of 15 to have sufficient quantities of sample. A pressure of about 170 kPa was applied. The quantities of CO_2 adsorbed were not directly measured but calculated from titration curves by which changes in alkalinity indicated how much bicarbonate was produced. It appeared that most of the captured carbonate remained in soluble form. The pH values attained were variable for the regular residue, with lowest values of about 7, while those for BAUXSOL™ were approaching 6. The equilibrium calcium concentration with calcite under these conditions is much too high for effective CO_2 mineralisation considering the large degree of dilution that was used. Thus, for the purpose of CO_2 mineral sequestration efficiency, these tests were not informative. The BAUXSOL™ did not show more carbon capture than the regular residue.

Saline wastewater that is generated from oil winning contains Ca^{2+} and Mg^{2+}. Research was done in the US using mixtures of aged residue from a Sherwin residue area with brine from a US oilfield [31]. A CO_2 partial pressure of about 170 kPa was applied. The amount of CO_2 sequestered does not increase through brine addition but rather reduces. The optimum brine-to-residue ratio is 10/90, providing near maximum sequestration, while the viscosity reduction was regarded sufficient for mixing to an acceptable carbonation rate. From the data provided in the paper, it is calculated that the CO_2 sequestration capacity in the testwork amounted to 18 kg CO_2/t BR (dry bauxite residue solids), which is not much better than achieved by others without such addition.

The most effective way of mineralising the excess of CO_2 available in the liquor would be by adding slaked lime. However, producing lime (CaO) involves burning limestone ($CaCO_3$) to drive off chemically bound CO_2 using fossil fuel, which results in more CO_2 emissions than is mineralised in residue carbonation. It is not only counterproductive but also expensive. Waste lime products, such as flue gas desulfurisation gypsum or lime kiln dust could be considered. However, the availability of these materials is limited, there are transportation costs and associated secondary CO_2 emissions and, in the case of desulfurisation gypsum, trapped impurities that would enter the residue liquor.

Gypsum ($CaSO_4\cdot2H_2O$) is a suitable calcium source that is readily available and not handicapped by high CO_2 emissions in its production since the emissions are restricted mainly to energy usages in mining and transportation. The release of sulfate renders the residue liquor unsuitable for return to the Bayer process; thus, loss of some otherwise recoverable soda will need to be factored in. But even without this cost factor, the process is not economic just based on the cost of gypsum alone. One tonne of CO_2 requires 172 (M.W. of gypsum) / 44 (M.W. of CO_2) = 3.9 tonne of gypsum. The price of crude gypsum delivered to site in the US ranges from 24 to 40 USD/t. Using a cost of 30 USD/t, as a fair estimate for gypsum delivered at the carbonation unit location, results in a cost of 3.9 x 30 = 117 USD/tonne of CO_2 mineralised, while the carbon credit obtained is 100 USD/tonne of CO_2 mineralised. This is just the cost for the gypsum and does not include e.g. the capital cost for gypsum storage and handling. Furthermore, in the production and transportation of gypsum 40 kg CO_2^e/t gypsum is emitted, thus 0.15-0.16 kg CO_2^e per kg CO_2 mineralised need to be deducted to account just for using gypsum alone.

In summary, there does not appear to be an economic solution for mineralising the CO_2 captured by the alkalinity associated with the sodium values in the residue liquor and the residue solids DSP. This poses a problem, because: (a) unproductive costs in flue gas compression capital investment and electric power usage are incurred, (b) secondary CO_2 emissions evolve from this compression electric power usage and (c) a heavily bicarbonated liquor has been produced which either needs to be causticised for return to the process or disposed of. The only potential advantage this liquor offers is the presence of soda extracted from the DSP cage. When recovered, it reduces the cost of plant caustic make-up, but this is at the expense of double the usual quantity of lime for causticising the liquor, since the soda is predominantly bicarbonated.

The quantities of captured CO_2 reported in the various publications on residue carbonation, were usually in the range of 20 to 45 kg CO_2/t BR [3,39]. These quantities were mostly established by either sample weight gain, or the reduction of CO_2 concentration in the artificial flue gas, or the increase in carbon content on samples dried at low temperature. Therefore, these quantities would have included sodium bicarbonate and sodium carbonate, either in solution or as solids in samples dried for the purpose of analysis. Those compounds do not qualify for carbon credit certification and bicarbonate is subject to release of most of the CO_2 once exposed to the low CO_2 partial pressure in the atmosphere, thus within a few days most captured CO_2 is lost. Genuine CO_2 mineralisation in the form of $CaCO_3$ was reported only occasionally. Judging by the XRF determined total CaO content of the residues, where such analyses were reported, it looks almost certain that actual CO_2 mineralisation was generally well below 20 kg CO_2/t BR.

4. FEASIBILITY

An overall assessment of the feasibility of residue carbonation for the alumina industry involves taking the following steps:

1. Establishing a Basis of Design (BoD) for developing a residue carbonation unit;
2. Determining the operating cost;
3. Determining the CO_2 emissions (CO_2^e) resulting from operating the carbonation unit;
4. Designing an actual residue carbonation unit for capital cost estimation.

The BoD intends to reflect the average capacity and operating data of a typical alumina refinery.

4.1 Basis of Design

Assumed is a refinery with a production capacity of 2 Mt/y smelter grade alumina (SGA), an operating factor of 94% and a residue factor of 1.2 t BR/t SGA. As a rough average a typical residue would contain about 3% CaO of which half would be in the form of TCA. This agrees with the lime consumption in alumina refining, which is typically 30-45 kg CaO/t SGA. Conversion to TCA is typically about 40-50%. Using 40 kg CaO/t SGA lime consumption, 45% conversion to TCA and said residue factor as broad averages yields 15 kg CaO as TCA/t BR, thus 1.5% CaO as TCA in the residue.

Furthermore, the following ballpark numbers are assumed for DSP in the residue: 10% SiO2 as sodalite, which corresponds with ~6.7-6.8% Na_2O. The Na_2O in the DSP cage, representing close to 25% of this value in digestion discharge sodalite, is for 45% associated with CO_3^{2-}, 25% with $Al(OH)_4^-$ and 5% with OH^-. 10% of these anions are washed out over the residue washers circuit and replaced by H_2O. It is assumed that under the pH conditions, agitation intensity and reaction time required for full TCA dissolution, the remaining $NaAl(OH)_4$ and NaOH in the DSP cage are fully extracted and Na_2CO_3 is for 50% extracted from the DSP cage.

An important process design parameter is the liquor/solids ratio (L/S). Experimental results suggest that the optimum L/S ratio is in the range of 0.4-0.6 as far as CO_2 capture is concerned [9, 40]. For CO_2 mineralisation it is not determined, but in Section 3.2.1 it has been reasoned that it should be as low as possible. From a practical point of view the L/S should be the minimum required to allow adequate mixing, but not much more, to minimise the quantity of highly carbonated residual liquor that the refinery would have to deal with post carbonation. Underflow of a high rate thickener last washer, having a typical L/S ratio of 0.70 (~59% solids), seems to be perfectly suitable.

The residue liquor analysis assumed is 11 g/L A as Al_2O_3, 19 g/L TC and 24 g/L TA, both expressed as Na_2CO_3. After TA extraction from DSP, the TA will be about 43 g/L.

Under these assumptions for a "typical" residue, and assuming an operating pH of around 8, whereby CO_2 is predominantly bound as HCO_3^-, the quantities of CO_2 captured and mineralised, once all TCA has reacted to $CaCO_3$, are calculated to be as shown in Table 1.

The quantity of CO_2 captured is 2.8 times the quantity of CO_2 mineralised. To put the latter quantity of 14 kg CO_2/t SGA in perspective: the quantity of CO_2 emitted from alumina refineries on average from the usage of fossil fuels is in the order of 800-900 kg CO_2^e/t SGA (2021).

Table 1. Total CO_2 capture and mineralisation per tonne of bauxite residue solids (BR) and per tonne SGA.

Form in which CO_2 is present post carbonation	kg CO_2 /t BR	kg CO_2/t SGA
Mineral CO_2 sequestration ($CaCO_3$)	11.8	14.1
Original liquor sodium CO_2 (mainly as Na^+ HCO_3^-)	12.2	14.7
DSP extracted sodium CO_2 (mainly as Na^+ HCO_3^-)	9.0	10.8
Total CO_2 capture	33.0	39.6

The CO_2 containing flue gas sources within alumina refineries are quite diverse. The calciners are one source, but because of the high water vapour content this source has not been considered. There are usually boilers on site, often in combination with steam turbines and/or gas turbines for cogeneration. Sometimes a refinery has a lime kiln on site, but this is a rarity apart from in China and Eastern Europe. Typical CO_2 contents of the various flue gas types are as follows:

Table 2. Typical volume % CO_2 in flue gas sources.

Flue gas	Gas turbine cogen	Natural gas boiler	Fuel oil boiler	Coal fired boiler	Lime kiln
Vol % CO_2	4	9	11	14	21

Two flue gases were selected for the evaluation: (a) from a gas boiler, and (b) from a lime kiln. The latter contains, besides fuel combustion CO_2, the CO_2 released from limestone. If, at some time in the future, alumina refineries would be fully electrified, then the exhaust from an electrified lime kiln would still be a source of CO_2 that could be captured and mineralised, thus with $CaCO_3$ going through a full circle via CaO and CO_2 back to $CaCO_3$ at the refinery site.

It is assumed that the flue gas is supplied to the compressor station at atmospheric pressure and at 60 °C. Water vapour content in both flue gases is below the saturation pressure of 20 kPa at this temperature. The ideal gas law is approximately applicable yielding a density of pure CO_2 of 1.61 kg/m^3. Therefore, the gas boiler flue gas contains 0.145 kg CO_2/m^3 and the lime kiln flue gas contains 0.338 kg CO_2/m^3. For the typical residue slurry used for the evaluation, 2.8 kg CO_2 needs to be captured for every kg of CO_2 mineralised. Using an absorption efficiency of 90%, it requires 21.5 m^3 of gas boiler flue gas or 9.2 m^3 of lime kiln flue gas at 60 °C to mineralise 1 kg CO_2.

4.2 Consumables Cost and Global Warming Potential

Residue carbonation goes along with electric power usage, largely for flue gas compression, but also for required residue slurry agitation and to a lesser extent for slurry pumping. Furthermore, in all cases there is loss of recoverable soluble alumina, because all the alumina has precipitated. If the carbonated liquor is not returned to the refinery, additional plant caustic make-up is required. If it is returned, the liquor must be causticised, necessitating increased lime consumption due to the predominance of bicarbonated soda and the soda extracted from the DSP. In the latter case savings are made in plant caustic make-up. All these consumables have a cost and their production and transportation to site have a so-called Global Warming Potential (GWP) which is the amount of CO_2^e emitted per unit consumable. For electric power and other energy sources often the term Scope 2 emissions is used, whilst for other consumables Scope 3 emissions is used.

Electric power is the most significant consumable in residue carbonation. The CO_2 emission for electric power generation depends on the energy source. For coal-based this is approximately 820 g CO_2^e/kWh, for natural gas-based 450 g CO_2^e/kWh, for nuclear 15 g CO_2^e/kWh (uranium mining and processing) and for renewable energy-based (hydro, wind, solar) it is roughly zero. A weighted average of these comes to 500 kg CO_2^e/MWh, a number also encountered in sustainability papers of a projective nature [41]. This value will likely reduce in the future. For the price of electricity, a US-based 2024 value of 65 USD/MWh is assumed.

The CO_2 emission from lime kilns consists of chemically released CO_2 from $CaCO_3$ and CO_2 from fuel combustion. Kiln energy is about 6.5–7.0 GJ/t CaO [42]. Assuming natural gas as the fuel source the combustion related emission is approximately 440 kg CO_2^e/t CaO. Including transportation energy and lime slaking power usage, the Scope 2 emission for slaked lime is approximately 500 kg CO_2^e/t CaO [43]. The release of the chemically bound CO in limestone has not been included, because causticising the carbonated residue liquor is roughly 100% efficient in the absence of soluble alumina in the liquor and the liquor TA being relatively low. Thus, the $CaCO_3$ in the kiln feed is returned to its original state. The price of lime delivered at site depends on the location and has been assumed to be 160 USD/t CaO (2024).

The net GWP effect of using lime in the refinery post residue carbonation is 500 kg CO_2^e/t CaO related to the fuel used in its production and delivery. Not only from an economic perspective, but also from a GWP perspective, it is therefore always best to reduce refinery lime consumption as much as possible. This reduces the TCA content in the residue thereby reducing its economic potential for CO_2 mineralisation, but it is still the better approach. If carbonation of residual TCA would then still be desired, it would be more efficient to carbonate the TCA containing waste streams separately instead of carbonating the entire residue, since TCA is (a) the only CO_2 mineralising constituent in the residue, and (b) it does not originate from the bauxite but has been added to the residue in the refinery process. Such a process is described in [37].

Caustic is mostly produced via the chlor-alkali membrane process, at least that is the case in Europe, where 85% is from membrane cells, 10% is from diaphragm cells and 5% is from other sources such as mercury cells [44]. The membrane process consumes about 2.25 MWh/t NaOH energy, predominantly as electric power [45]. This yields a GWP of 1125 kg CO_2^e/t NaOH, which agrees with the CarbonCloud published value of 1120 kg CO_2^e/t NaOH. Taking shipping, railing and unloading into account an estimated value of 1250 kg CO_2^e/t NaOH is assumed. The prices that alumina refineries pay for their caustic are obviously not in the public domain, but a typical price is believed to be 260 USD/t NaOH FOB. Including the cost for transport and handling a cost of 275 USD/t NaOH (2024) has been assumed.

The Scope 2 GWP for alumina refining can be calculated using world average energy source data published by the IAI in 2021 [46] and typical GWP values for the various energy sources, see Table 3. Energy related GWP for bauxite mining works out to be approximately 28 kg CO_2^e/t SGA on average. Adding a similar amount for bauxite shipping yields approximately 950 kg CO_2 /t SGA. This excludes the Scope 3 GWP contributions of consumables such as caustic and lime. The latter two add an estimated 150 kg CO_2^e/t SGA, making a total of 1100 kg CO_2^e/t SGA. In view of on-going electrification and fuel switching to natural gas at the expense of coal a GWP value of 900 kg CO_2^e/t SGA has been assumed for the near future. A projected long term alumina price of 360 USD/t SGA has been used. Applying these numbers, it has been estimated that the recoverable soluble alumina that is lost through residue carbonation at the backend of the residue washing circuit has a GWP of 400 kg CO_2^e/t SGA and a value of 200 USD/t SGA at that point in the refinery circuit.

Table 3. Energy related (Scope 2) GWP for alumina refining in 2021. The total GWP for alumina production is estimated at 1100 kg CO_2^e/t SGA inclusive of the GWP of the major consumables: bauxite, caustic and lime.

World average distribution of energy sources (2021)	%	kg CO_2^e/GJ
Coal	52.7	97
Natural gas	29.5	53
Fuel oil	7.8	75
Electricity	7.4	139
Other	2.5	pro rata assumed
World average energy consumption (2021)	**GJ/t SGA**	**kg CO_2^e/GJ**
Refinery process, energy related	10.5	895

4.3 Dealing With Post-Carbonation Liquor

The development of residue carbonation technology covers two parts:
1. Deciding what to do with the residual liquor;
2. Designing the actual residue carbonation unit.

The residual carbonation liquor is loaded with bicarbonate and has a relatively low pH. It takes days for the bicarbonate to convert back to carbonate once the liquor is exposed to atmospheric CO_2 partial pressure, as demonstrated in numerous pH rebound experiments. One could consider building reservoirs or residue lakes for providing residence time to the liquor and perhaps apply aeration to speed up the pH rebound. But even if such a capital-intensive solution would be applied there is additional carbonate present from the free caustic and aluminate in the original liquor and from the alkalinity in the DSP. Through mud farming and temporary storage in the residue disposal area, some conversion back to carbonate will occur. Returning the liquor, pH rebounded or not, to the refinery process would drive the causticity (TC/TA or C/S) of the process liquor down, and therewith plant liquor productivity. Two options have been considered for dealing with the carbonated residue liquor:

Option 1: Disposal with the residue to a residue disposal area with enhanced evaporation (e.g. through mud farming) and subsequent disposal of any remaining runoff to the environment through an effluent treatment system. The originally recoverable soluble soda is lost and requires additional NaOH make-up. As a compensation, less lime is used in side stream causticisation.

Option 2: Causticise all soda, including the liberated soda from DSP, and return to the refinery process. The liberated chemical soda from the DSP reduces NaOH make-up, but extra lime is required because all the soda in the liquor is in the bicarbonated state. A potential issue is the return of certain impurities sequestrated in TCA and DSP to the refinery process, such as fluoride.

In both options the original soluble alumina has precipitated and is therefore lost. The options are diagrammatically shown in Figure 5. Post carbonation, the slurry is filtered in membrane press filters in the case of Option 2 (NB: in principle run-off from the residue disposal area could also be used in this option), or simply disposed of to the residue disposal area without run-off return in the case of Option 1, with effluent treatment and disposal if necessary. Table 4 presents the outcome of the evaluation of both options. Option 2 is favoured, especially in terms of GWP, but the risk of recycling e.g. oxalate, fluoride and possibly other harmful impurities back to the refinery process would have to be dealt with.

Figure 5. Managing post-carbonation residue liquor, heavily loaded with bicarbonate

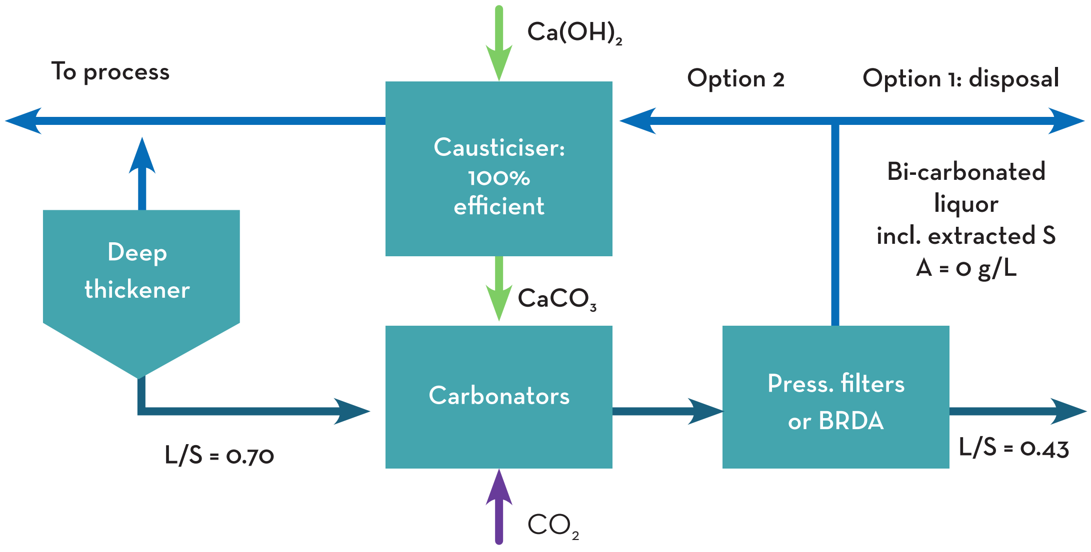

Table 4. The economics of two options of dealing with post-carbonation liquor.

Cost data USD/t BR kgCO_2	%	kg CO_2^e/GJ
Option 1: Disposal	0.29	0.59
Loss of otherwise recoverable dissolved Al_2O_3	0.29	0.59
Replacement of originally recoverable TA with NaOH	1.33	6.03
Saving lime in normal side stream causticisation	-0.11	-0.35
Net cost of Option 1	1.51	6.26
Option 2: Recover		
Loss of otherwise recoverable dissolved Al_2O_3	0.29	0.59
Saving NaOH because of liberated TA from DSP	-1.11	-5.02
Extra lime for causticising bicarbonate liquor with also extra TA	1.87	5.84
Net cost of Option 2	1.05	1.40
Option 1 - Optoin 2	0.45	4.86

4.4 Carbonation Unit Design

Various systems have been suggested and studied in the literature for contacting the residue with the flue gas. In one system, last washer overflow is counter currently contacted with flue gas in a packed tower and, being loaded with bicarbonate, circulated back to the washer [47]. There are several drawbacks with such a system. Dissolved alumina in the liquor in contact with acidic CO_2 will cause severe scaling of the packing, requiring frequent packing replacement for caustic washing. In the absence of mixing in the washer, and the liquor being exposed to the atmospheric CO_2 partial pressure again (causing some degree of rebound), it is unlikely that much CO_2 mineralisation takes place. The absence of agitation is also a handicap, also for fixed bed columns filled with residue, which has been the subject of several research studies [3, 20]. The same applies to moving bed reactors for continuous operation.

An important aspect of the design is the reaction rate. It concerns two overlapping reactions in series: (a) liquor carbonation, and (b) CO_2 mineralisation. Various researchers established that the liquor carbonation rate increases with CO_2 partial pressure [1, 7, 17]. It has also been found that the carbonation rate increases with stirrer speed and with increased bubbling flue gas flow rate [1, 3]. This indicates that the liquor carbonation rate is mass transfer limited. Batch experiments with residue liquor in the absence of solids show a slowdown of the pH reduction rate between pH 10.5 and 9.5. This buffering is caused by $Al(OH)_3$ precipitation. In the presence of residue solids the buffering is more pronounced, presumably because of the dissolution of alkalinity from TCA and DSP as well as the consequent precipitation of more $Al(OH)_3$. Hence the time required for CO_2 absorption depends on these slow solids dissolution reaction rates.

The CO_2 partial pressure should not exceed a threshold above which the equilibrium calcium concentration with calcite starts to rise exponentially. As explained in Section 3.2.1, this is dependent on the liquor TA. For a typical high-rate thickener last washer underflow, as per the BoD, the TA in the residue liquor would rise to about 43 g/L after dissolution of the alkalinity from the DSP. The threshold CO_2 partial pressure before the equilibrium calcium concentration starts to rise is then in the order of 1000 kPa (abs), see Figure 4b. For 9% CO_2 in flue gas this would correspond to approximately 11 MPa total flue gas pressure and for a 21% CO_2 flue gas to approximately 4.8 MPa. The pH would be close to 7, but a 10-fold lower pressure, which brings the pH down to around 8, would already be sufficient for TCA dissolution and CO_2 capture. Under adequate agitation and flue gas dispersion, the required liquor carbonation time under such pressure is estimated at 15 minutes. At slightly above atmospheric pressure (at the residue suspension surface) the liquor carbonation time would be in the order of 20 to 25 minutes.

The required time for full CO_2 mineralisation with the available calcium is longer than 25 minutes. From carbonation experiments where carbonation of dry residue solids was compared with carbonation of residue slurry it is evident that the presence of liquor reduces the CO_2 mineralisation time [9]. Here, agitation was also essential for getting an acceptable mineralisation rate, but the time required often still exceeded one hour or even two hours. In non-bauxite residue research on carbonation reaction mechanisms there are reports on calcium carbonate precipitation on the surfaces of calcium minerals hindering the calcium dissolution rate from those minerals [48,49]. Although such passivation has not been investigated in bauxite residue carbonation, it could very well also play a role here, especially since the carbonation rate tends to slow down on the progression of carbonation. Given the experience in other areas of CO_2 mineralisation, the possibility of passivation should be taken into account. Not only Ca^{2+} needs to travel from the TCA bulk through the calcite layer, but also the $Al(OH)_4^-$ counter ions that supply part of the alkalinity involved in the CO_2 capture, need to travel through that layer as well, since charge neutrality must be kept. However, at the prevailing reduced pH conditions, the aluminate ions will precipitate as $Al(OH)_3$, which may create another obstacle to TCA dissolution besides the calcite formation.

Apart from mixing for solids suspension, gas bubble dispersion and accelerated mass transfer of $CO_2(aq)$ through the solution, it would be opportune at the same time to increase the mixing to an extent that allows scouring of particles amongst themselves and against the reactor walls and internal surfaces to minimise said passivation. The type of equipment well suited for such duty is the attrition scrubber. The proposed design for a residue carbonation unit includes reactors equipped with attrition scrubbers. Although no experimental work was found in the literature on the application of attrition scrubbers in mineral carbonation, it is anticipated that the CO_2 mineralisation time could be reduced from being at least one hour to an optimistic 30-40 minutes. It not only reduces reactor volume but it also ensures that all reactive calcium is able to dissolve.

The gas volume has a large, determining impact on the reactor volume. For a typical 2 Mt/y alumina refinery it was found that 5-7 reactors in series generally yielded sensible reactor sizes.

This also solved a practical problem encountered, namely that in the case of one reactor the residence time for liquor carbonation (determined by the gas flow) would have to be the same as for CO_2 mineralisation (determined by the residue slurry flow), unless the reactor would be compartmentalised. Since the residence time for liquor carbonation is smaller than for CO_2 mineralisation, a single reactor would be sized on the basis of a too large gas volume. It is proposed to design the reactor system in a way providing sufficient time for liquor carbonation in say 3-4 reactors with the reactor volume being largely determined by gas volume and the supplementary 2-3 reactors providing the additional time required for completing the CO_2 mineralisation under a substantially reduced gas volume.

4.5 Capital Cost and Operating Cost

A useful source of information on capital cost for carbonation projects is a thesis by Huijgen [50], who made use of information from the DACE price booklet [51] and regarding e.g. scale factors from experts in this field [52, 53]. Although an increased pressure reduces the reactor volume, the reactor wall thickness increases. Based on Huijgen, the capital cost scale factor for pressure is approximately exponent 1.6, while that for volume is approximately exponent 0.45. Since p x V can be assumed to be roughly constant and reactor volume is largely determined by the gas, it follows that reactor capital cost is roughly proportional to pressure to the power 1.15 for a given gas mass flow rate. Although the carbonation time reduces with increasing pressure, this dependency on pressure appears to be moderate, so that the capital cost for the reactor vessels will still increase with increasing pressure. In addition, the capital cost of a gas compressor is proportional to the volumetric gas flow rate at the suction to the power 0.72, which in the BoD for a specific flue gas quality is constant at a given CO_2 mineralisation duty. The motor capital cost is approximately proportional to the compressor motor power rating to the power 1.17. Compressors and reactor vessels become more expensive with increasing pressure. Thus, without needing any sophisticated calculations, it can be concluded that from a capital cost point of view a low pressure is preferable. This is also true for operating cost, where the electric power for gas compression is the major consumable in residue carbonation. The power consumption can be estimated using the following formula for the power required to compress one cubic meter of gas adiabatically from p_{in} to p_{out}:

$$E = \frac{z}{\eta} \cdot \frac{k}{k-1} \cdot P_{in} \cdot [(P_{out}/P_{in})]^{(k-1)/k} - 1] * V / 3600 \qquad (11)$$

where:

E	energy, kWh/m^3
p	pressure, kPa
V	volume m^3 at temperature
k	c_p / c_v = 1.4 since considerable part of the flue gas is air
Z	compressibility factor = 1 since this generally applies roughly in such systems
η	efficiency factor = 0.90 for such compressors

The minimum compressor discharge pressure required is estimated to be 450 kPa (abs) to overcome residue slurry static head in the reactors, the pressure drop over the required gas distribution plates in reactor bottoms and over the demisters in reactor exhausts, as well as other hydraulic losses. The suction pressure is assumed to be atmospheric, 101.325 kPa (abs).

For these pressures, formula (11) produces 0.0581 kWh/m^3 gas. In Section 4.1 the required volume (m^3) of flue gas for mineralising 1 kg CO_2 has been calculated and Section 4.2 specifies the cost and GWP of 1 kWh electricity. It follows that for a 9% CO_2 flue gas the power consumption, power cost and Scope 2 GWP for mineralising 1 tonne of CO_2 are 1.25 MWh, 81 USD and 0.62 t CO_2^e respectively. Thus, the cost per net tonne of CO_2 mineralised is 216 USD against a projected carbon credit of 100 USD. The net result for a 21% CO_2 flue gas is 47 USD. This is for compression power usage alone.

Increasing the discharge pressure always leads to increased power consumption and therewith to increased electricity cost and Scope 2 emissions. The net quantity of CO_2 mineralised thus decreases, while the cost for electricity increases. This is depicted in Figures 6 and 7, which show (a) compression power requirement and related Scope 2 CO_2 emission per tonne of CO_2 mineralised for the two qualities of flue gas evaluated, supplied at atmospheric pressure at 60 °C, as a function of discharge pressure, and (b) the associated cost per tonne CO_2 mineralised before and after deduction of the Scope 2 CO_2 emission, and the projected revenue in carbon credits for comparison. It is always more economical to apply a low, but still practical pressure. Using high pressure not only puts at risk CO_2 mineralisation from a chemistry point of view, but it is economically unfavourable from both a capital cost and operating cost point of view.

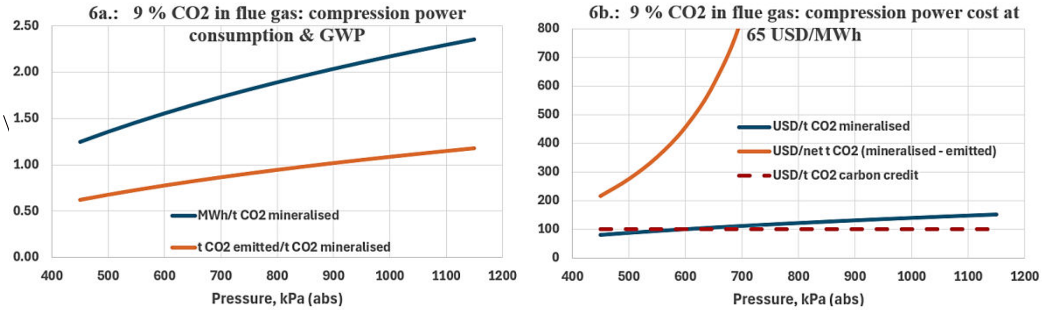

Figure 6. Compression of a 9% (v/v) CO_2 flue gas – effect of discharge pressure on:
(a) power requirement and Scope 2 CO_2 emission per tonne CO_2 mineralised;
(b) power cost per tonne CO_2 mineralised without and with Scope 2 emission deduction.

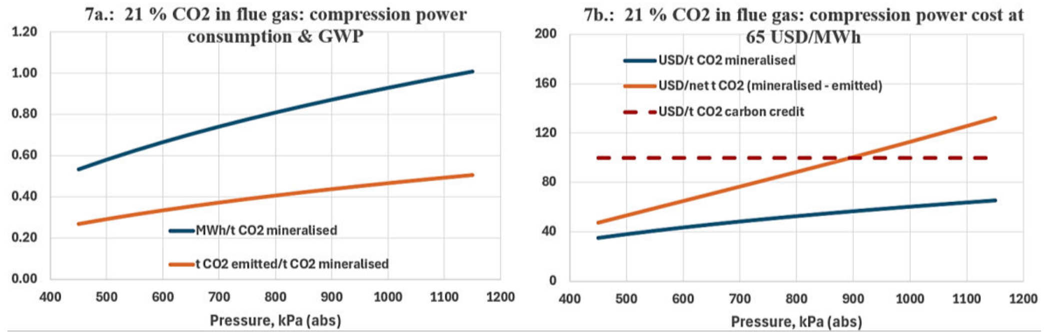

Figure 7. Compression of a 21% (v/v) CO_2 flue gas – effect of discharge pressure on:
(a) power requirement and Scope 2 CO_2 emission per tonne CO_2 mineralised;
(b) power cost per tonne CO_2 mineralised without and with Scope 2 emission deduction.

One could consider enriching a flue gas to high CO_2 concentration. Two technologies widely used for this purpose are amine scrubbing and membrane separation. Membrane separation has gained more prominence over the past decade, because of lower capital cost, modular design, compact footprint and ongoing development of suitable polymers. Both methods require energy, namely for solvent regeneration in the case of amine scrubbing and for gas compression in the case of membrane separation. Membrane technology would be preferred for lower cost and lower GWP. However, operating costs are in the order of 50 USD/t CO_2, and GWP in the order of 75 kg CO_2^e/t CO_2. Therefore, the upfront operating costs, capital cost and Scope 2 emissions of flue gas CO_2 enrichment are not expected to add value.

Apart from power consumption for gas compression, there is power consumption for the attrition scrubbing type agitation to overcome TCA passivation and promote reactants mass transfer. The power consumption based on a 59% solids washer underflow (L/S = 0.7) will be in the order of 5 kW/m^3 slurry. At 40 minutes residence time the power consumption per tonne CO_2 mineralised is 0.28 MWh at a cost of 18 USD and 0.14 t CO_2^e Scope 2 emission.

The major items of equipment for a residue carbonation unit are the compressors, the compressor motors and the reactor vessels. Capital cost and scaling factors for these items were taken from Huijgen [50], who used information from [51–53]. This included capital cost scaling factors for reactor vessel volume and pressure and compressor volume flow and discharge pressure. The design compressor discharge pressure was chosen to be the minimum estimated to overcome system losses, namely 450 kPa (abs). A higher pressure always leads to a higher capital cost for compressors and reactor vessels and a higher operating cost.

The resulting prices were converted from euros to US dollars at a rate of 1.10 USD/EUR and escalated from 2004 to 2024 by applying a US building materials and supplies index of 1.88. Subsequently, scaling factors for direct cost (equipment erection, instrumentation, piping, process buildings, storage, utilities etc.) and indirect cost (design & engineering, contractor's fee, contingency) were applied to arrive at the overall installed cost, and 10% was added for working capital. For the inclusion of direct cost, indirect cost and working capital, a multiplication factor of 4 was applied to the major equipment items. A carbonation unit availability of 95% was optimistically assumed. Option 2 for post carbonation liquor treatment was selected. For causticisation and upgrading of lime slaking, an installed cost of 25 MUSD was assumed. The operating cost and GWP values for Option 2 specified in Table 4 were used as well as those for the electric power consumed in flue gas compression and agitation. The results are summarised in Table 5. Note that items such as labour cost and maintenance cost are not included.

Table 5. The economics of bauxite residue carbonation of the BoD typical alumina refinery

Flue gas volume % CO_2		**9%**	**21%**
Total capex	MUSD (2024)	57.0	42.3
Tonne CO_2 mineralised per year	t CO_2/annum	26864	26864
Capex/annual tonne CO_2 mineralised	USD/annual tonne	2121	1576
El. power cost for compression + agitation	USD/t CO_2 miner.	99	53
Net cost for lost alumina + lime - caustic	USD/t CO_2 miner.	90	90
Capex/10 years + opex per t CO_2 miner.	USD/t CO_2 miner.	401	300
Scope 2 t CO_2^e/t CO_2 mineralised	t CO_2^e/t CO_2 miner.	0.76	0.41
Scope 3 t CO_2^e/t CO_2 mineralised	t CO_2^e/t CO_2 miner.	0.12	0.12
Net tonne CO_2 mineralised per year	Net t CO_2/annum	3140	12718
Capex/10 years + opex per net t CO_2 miner	USD/net t CO_2 miner.	3431	634

5. CONCLUSIONS

Table 5 demonstrates that even with an interest free capital cost payback time of 10 years and having a lime kiln on site, the carbon credit price should be at least 700 USD/t CO_2 for bauxite residue carbonation to have some chance to be economically feasible, while the projection is a price of 100 USD/t CO_2. For the case of flue gas from a natural gas fired boiler, the economics are much more difficult at > 3000 USD/t CO_2 for obtaining cost neutrality. Regardless, it would make more sense to carbonate the waste lime streams that contain TCA rather than the entire bauxite residue stream to which these lime streams are added. Even better is to reduce the formation of TCA in the Bayer process all together since this will reduce the plant lime consumption and therewith the CO_2 emissions of burning $CaCO_3$ in lime kilns (chemically bound CO_2 as well as fuel combustion CO_2).

From a process technical perspective as well as an economic perspective it appears best to design an alkaline waste CO_2 mineral sequestration unit for the lowest practical pressure and lowest practical (e.g. with respect to agitation) L/S ratio. Dilution should always be avoided.

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