

NATURAL REMEDIATION OF ALKALINE CONTAMINATION OF GROUNDWATER THROUGH BUFFERING: IMPLICATIONS FOR MANAGEMENT

Gerritse, RG¹, Thomas, GA^{2*}

¹ *Geoprocc, Wembley Downs, Western Australia*

² *Alcoa World Alumina Australia, Booragoon, Western Australia*

Abstract

At alumina refineries worldwide, there is the potential for contamination of groundwater by alkaline process fluids (caustic soda, Bayer liquor, bauxite residue leachate). Sources are leaks in containment areas for refinery operations and for bauxite residue, and spills on soils in unsealed areas with subsequent infiltration and leaching to groundwater. Alkaline contamination of the receiving groundwater not only increases pH and alkalinity of the groundwater but also results in associated increases in concentrations of certain trace elements. In particular groundwater concentrations of anions such as fluoride and (hydr)oxyanions such as arsenate and aluminate can rise rapidly with increasing alkaline pH.

Solution alkalinity and CO₂ pressure are the main determinants of pH. Increases in groundwater pH can be buffered naturally by high CO₂ pressures, by ion-exchange with clays, by precipitation as Ca and Mg carbonates or hydroxides in saline waters and also by H₂SO₄, generated from oxidation of pyrite on lowering of the water table. The relationship between pH, alkalinity and CO₂ pressure is discussed, both in the presence and absence of calcite, which is a key component of limestone formations.

Effects of ion exchange, precipitation and pyrite oxidation become apparent when molar increases in solution concentrations of Na and alkalinity from NaOH are not equal. Examples are presented of these buffering processes as observed for groundwater affected by alkaline process fluids at the three Alcoa World Alumina refineries in Western Australia: Kwinana, Pinjarra and Wagerup. Implications of these alkaline buffering processes for the management of alkaline groundwater contamination are discussed. It is concluded that long term management of impacts of alkaline contamination on groundwater quality can benefit from an understanding of hydrochemical and geochemical reactions in groundwater systems, such as occur through: elevated CO₂ pressures; ion-exchange with clays; precipitation of Ca and Mg carbonates or hydroxides in groundwater, especially saline waters; and H₂SO₄ generated from oxidation of pyrite.

1 Background

At alumina refineries worldwide, there is the potential for contamination of groundwater by alkaline process fluids (caustic soda, Bayer liquor, bauxite residue leachate). Major sources are leaks in containment areas for refinery operations and for bauxite residue and spills on soils in unsealed areas with subsequent infiltration and leaching to groundwater.

2 Trace elements

Alkaline contamination of groundwater increases alkalinity and pH, resulting in rising concentrations of many trace elements. Solubilities of most trace elements are strongly dependent on alkalinity and pH, mainly through dissolution of and/or desorption from aquifer materials. In particular groundwater concentrations of anions such as fluoride and of (hydr)oxyanions such as arsenate and aluminate can rise rapidly with increasing alkalinity and pH.

Results of monitoring groundwater at the Kwinana and Wagerup alumina refineries of Alcoa in Western Australia for As and F are plotted in Figure 1 against pH and alkalinity. Results are compared with concentrations expected for conservative mixing (=no adsorption to aquifer materials or other reactions) of As, F and alkalinity in groundwater and bauxite residue leachate (BRL).

Concentrations of As and F in groundwater increase with pH and alkalinity and at higher concentrations are commonly less than expected from conservative mixing with BRL. This suggests that concentrations of

As and F in groundwater are the result of desorption of their anions from aquifer materials by HCO₃⁻, OH⁻ and CO₃²⁻, which dominate alkaline contaminated groundwater, rather than of advection from contaminant sources such as BRL. Only where groundwater has been directly contaminated or subjected to intensive abstraction near contaminant sources (e.g. by recovery bores) will concentrations follow the expected trend for conservative mixing with BRL.

Increases in groundwater pH can be buffered naturally by: high CO₂ pressures; ion-exchange with clays; precipitation of Ca and Mg carbonates or hydroxides in saline waters; and H₂SO₄, generated from oxidation of pyrite, when exposed on lowering of the water table.

3 pH and CO₂

In Figure 2, CO₂ pressures and pH measured in groundwater, sampled at the Kwinana and Wagerup refineries, are plotted and compared with theoretically calculated relationships. The plots clearly demonstrate the importance of the buffering effect of elevated CO₂ pressure on groundwater pH and thus the natural remediation of groundwater contaminated by alkaline refinery process fluids. Alkaline contaminated groundwater at the Wagerup refinery is commonly less than 0.01 M NaOH, equivalent to about 2.5% bauxite residue leachate (BRL). At the Kwinana refinery a number of groundwater samples indicate contamination of up to between 0.1 and 0.2 M NaOH.

Groundwater concentrations of Na in excess of what can be expected from a marine Na/Cl ratio should be equal on a molar equivalent basis

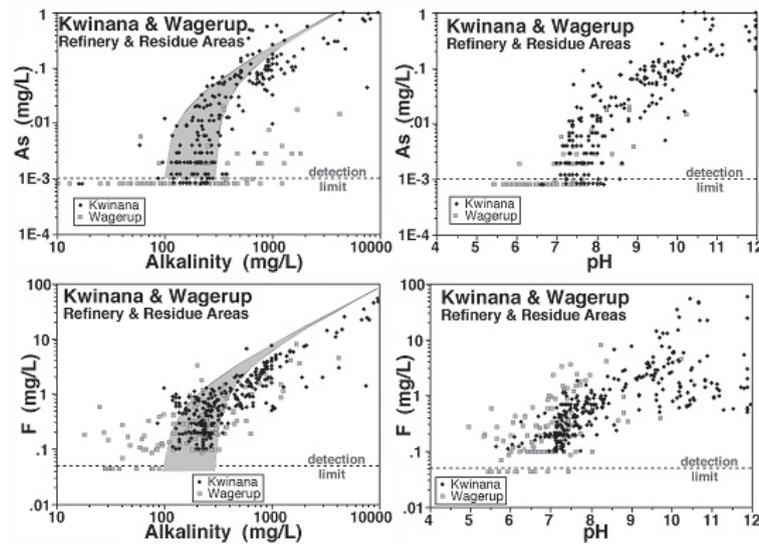


Figure 1. Log-log plots for groundwater concentrations of As and F against alkalinity and pH at the Kwinana and Wagerup refineries of Alcoa in Western Australia. Data are compared with ranges (bounded grey areas) calculated for mixing of background quality groundwater with bauxite residue leachate from the refineries, assuming no adsorption, precipitation or other reactions.

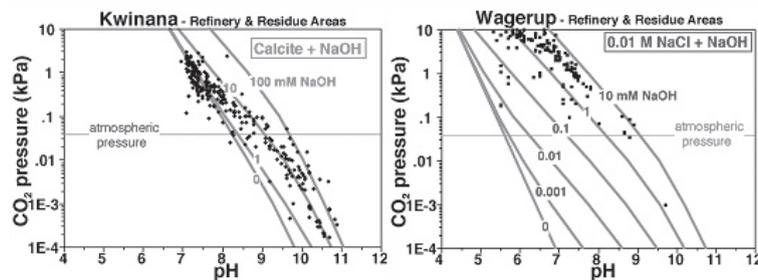


Figure 2. Plots against pH of CO₂ pressures, calculated for equilibrium with surficial groundwater at the Kwinana and Wagerup refineries of Alcoa in Western Australia. Sample data are compared with theoretical relationships (curves) for equilibrium with calcite (Kwinana) or with 0.01 M NaCl (Wagerup) and varying amounts of added NaOH.

to the associated increases in alkalinity, when the excess is derived from NaOH in refinery process fluids. This is explored in Figure 3, where the excess concentration of Na is calculated from: $[Excess\ Na] = [Na^+] - 0.86 [Cl^-]$, [] denoting concentration and 0.86 the molar ratio of Na⁺/Cl⁻ in ocean water.

Slopes for equal molar equivalent increases of [Excess Na] and [Alkalinity] are shown in the plots. Deviations commonly occur on either side of the slopes as a result of reactions of clays with Na⁺ and reactions reducing or generating alkalinity. These reactions are indicated in Figure 3 and discussed below.

4 Ion-exchange

Smectitic clays (montmorillonite) occur in aquifer materials at the Wagerup and Pinjarra refineries and adsorb increases of Na⁺ ions in exchange for H⁺, Ca²⁺ and Mg²⁺ ions. In addition OH⁻ ions from NaOH can scavenge H⁺ ions from silanol (Si-OH) and aluminol (Al-OH) groups at the clay surface (Bourg et al. 2003), apparently buffering pH and increasing the adsorption capacity for Na⁺, explaining negative 'excess Na' concentrations. Increasing pH and Ca and Mg can result in precipitation of Ca/Mg carbonates.

5 Precipitation of Ca/Mg carbonates and sulphate reduction in saline groundwater

At the Kwinana refinery, ocean water from the nearby Indian Ocean infiltrates along the base of the surficial aquifer as a saline wedge extending up to 1 km inland. Ca and Mg are precipitated as carbonates where alkaline contaminated groundwater mixes with water from

the saline wedge. In the saline wedge concentrations of SO₄²⁻ relative to Cl⁻ in alkaline contaminated samples commonly decrease through sulphate reduction. This generates an equivalent increase in alkalinity, counteracting to some extent the loss of alkalinity from precipitation of Ca and Mg carbonates. Contaminant anions such as As can be coprecipitated with Ca/Mg carbonates (Roman-Loss et al. 2003, Romero et al. 2004). For refineries in coastal environments, the saline wedge can play an important role in the natural remediation of groundwater from contamination by alkaline process fluids.

6 Pyrite oxidation – Fe reduction

Deposits of pyrite (FeS₂) are common in aquifers in the coastal plain on which the Kwinana, Wagerup and Pinjarra refineries are situated. Deposits in the aquifer are characterized by a reducing groundwater environment, but on lowering of the groundwater table, e.g. through seasonal factors and/or groundwater abstraction, pyrite is exposed to oxygen and generates acidity according to (Peiffer & Stubert 1999): $FeS_2 + 15/4 O_2 + 5/2 H_2O \rightarrow 2 H_2SO_4 + FeOOH$. Concentrations of SO₄²⁻ in groundwater in excess of what can be expected from a marine SO₄²⁻/Cl⁻ ratio are equal on a molar equivalent basis to the associated decreases in alkalinity from H₂SO₄.

In the absence of pyrite, reducing conditions in alkaline contaminated groundwater can lead to microbially mediated oxidation of organic matter through reduction of ferric (hydr)oxides, generating alkalinity: $4 FeOOH + CH_2O + H_2O \rightarrow 4 Fe^{2+} + CO_2 + 8 OH^-$.

The combined effects of pyrite oxidation or Fe reduction, sulphate reduction and ion-exchange are illustrated in Figure 4, where concentrations of 'excess Na' measured in groundwater, sampled at Residue

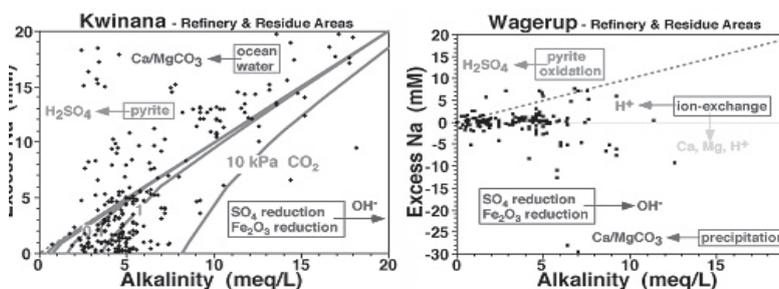


Figure 3. Plots of concentrations of 'excess Na' (from NaOH) against alkalinity in surficial groundwater, sampled at the Kwinana and Wagerup refineries of Alcoa in Western Australia. Sample data are compared with theoretical relationships in the absence of reactions (other than with CO₂) affecting [Na⁺] and/or [alkalinity] for a calcitic (Kwinana: lines/curves) or non-calcitic environment (Wagerup: dashed line).

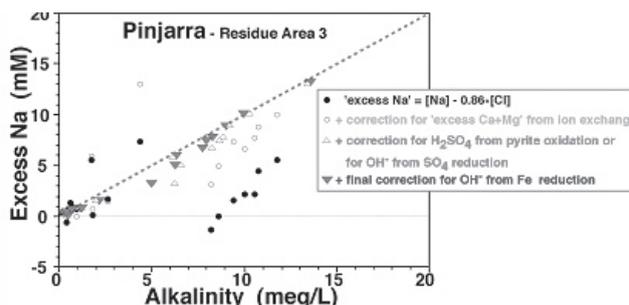


Figure 4. Plot of concentrations of 'excess Na' (from NaOH) against alkalinity in alkaline contaminated groundwater at the Pinjarra refinery, before and after correcting for contributions of ion-exchange, pyrite oxidation, SO₄²⁻ reduction and of Fe reduction.

Drying Area 3 of the Pinjarra refinery, are plotted against alkalinity. The initial concentrations of 'excess Na' are then corrected for ion-exchange by adding the 'excess' molar equivalent concentrations of Ca and Mg (assuming no precipitation). Alkalinities are corrected in a similar way for 'excess SO₄⁻', assuming it to have resulted from pyrite oxidation (positive excess) or from sulphate reduction (negative excess). This correction appears to particularly affect two groundwater samples with low alkalinity. Finally the alkalinity generated from Fe-reduction is corrected for, assuming the measured solution concentrations of Fe to be Fe²⁺. Data in Figure 4 clearly show that reactions in aquifers can add to as well as subtract from groundwater as much alkalinity as contributed

by leaching of diluted refinery process fluids and should be considered in any groundwater remediation strategy.

7 Conclusions

Long term management of impacts of alkaline contamination on groundwater quality can benefit from an understanding of hydrochemical and geochemical reactions in groundwater systems, such as occur through: elevated CO₂ pressures; ion-exchange with clays; precipitation of Ca and Mg carbonates or hydroxides in groundwater, especially saline waters; and H₂SO₄ generated from oxidation of pyrite.

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