Mine Water and the Environment (2001) 20: 122–128 © IMWA Springer-Verlag 2001

Technical Article

Prevention of Acidic Groundwater in Lignite Overburden Dumps by the Addition of Alkaline Substances: Pilot-scale Field Experiments

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Abstract. Mining activities in the Rhineland lignite mining area in Germany have led to increased mineralisation and acidity of groundwater due to the oxidation of sulfide minerals. The potential benefit of adding alkaline substances (crushed limestone and a mixture of fly ash and crushed limestone) to the overburden spoil was investigated using laboratory columns and pilot-scale field experiments. The latter tests were each conducted with 13 metric tons of overburden. A considerable improvement in water quality (decreased sulfate, iron, trace elements and acidity) was found in both scales of experiment. Similar improvements are expected in the limed overburden dump of the Garzweiler lignite mine.

Key Words: Acid mine drainage, alkaline addition, fly ash, Germany, groundwater, hydrogeochemical calculations, lignite mining, limestone, prevention, water chemistry

Introduction

The Rhineland area is the most important lignite mining district in Germany, with a production of 97.4 million tons of lignite in 1998 (Rheinbraun AG 1999). In order to mine lignite in open pits, aquifers must be dewatered by pumping and the overburden must be excavated. The overburden is mostly of Tertiary age and often contains sulfide minerals. For instance, the overburden of the northernmost open pit, Garzweiler, has an average pyritic sulfur content of 0.26 wt % (Van Berk and Wisotzky 1995; Wisotzky 1998a, 1998b, 2000.) Due to mining, the sulfide minerals (mostly pyrite) are partially oxidized (Equation 1,2; Singer and Stumm 1970).

$$FeS_{2(s)} + 7/2O_2 + H_2O \Rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad \text{(Eq 1)}$$

$$FeS_{2(s)} + 15/4O_2 + 1/2H_2O \Rightarrow Fe^{3+} + 2SO_4^{2-} + H^+ \qquad \text{(Eq 2)}$$

Both infiltrating water and rising groundwater leach the pyrite oxidation products ($Fe^{2/3+}$, SO_4^{2-}, H^+) from pore water and dissolve secondary iron sulfate minerals like melanterite, rozenite and jarosite (Wisotzky 1994), causing mineralisation and acidification of groundwater and surface water discharge. For example, the groundwater at the abandoned Berrenrath dump, in the southern part of the mining district, has a sulfate concentration of up to 7000 mg/l and a ferrous iron concentration of up to 3500 mg/l, with a pH as low as 4.5 (Van Berk and Wisotzky 1995). The dominance of these oxidation products becomes obvious when discharging groundwater comes into contact with atmospheric oxygen, precipitating iron oxihydroxides and decreasing pH (Schultze et al. 1999; Wisotzky 2000).

Deterioration of water quality due to pyrite oxidation is observed not only in the Rhineland lignite mining area but also in the Lusatian and Central German lignite mining districts. Different remedial strategies are being pursued in these areas. In the latter, the primary research approach is the addition of degradable organic substances to cause sulfate reduction (Blodau et al. 1998; Fyson et al. 1998; Friese et al. 1998; Wisotzky 1998b; Wisotzky and Kringel 1998). In the Rhineland mining district, the addition of alkaline substances (crushed limestone or a mixture of fly ash and crushed limestone) to the overburden before dumping has been intensively investigated (Kringel 1998; Wisotzky and Kringel 1998; Obermann and Wisotzky 1998).

Since 1998, crushed limestone has been added to the overburden at the Garzweiler open pit in an effort to neutralise the overall acidity (sulfide and metal acidity, Equations 3, 4, 6-10) and to precipitate partially the dissolved sulfate as gypsum ($CaSO_4{*}2H_2O$, Equation 5). Additionally, the removal of dissolved iron, by precipitation of ferrous iron carbonate (siderite, Equation 6) and/or iron oxihydroxide minerals (e.g. $(FeOH)_3$, Equations 7, 8), is desired to prevent acidification by aeration. The associated trace elements (mainly Co, Ni, Zn, As, Al) should also be removed from the water by sorption and precipitation (e.g. Equations 9, 10). Overall, the addition of alkaline substances should ensure that the groundwater has a near-neutral pH and is low in iron and trace elements.

The following equations show the anticipated reactions with crushed limestone and fly ash (in which the main alkaline substance is $Ca(OH)_2$):

$3/2H^+ + CaCO_{3(s)} \Leftrightarrow Ca^{2+} + 1/2HCO_3^- + 1/2CO_2 + 1/2H_2O$ (Eq 3)

$2H^+ + Ca(OH)_{2(s)} \Leftrightarrow Ca^{2+} + 2H_2O$ (Eq 4)

$SO_4^{2-} + Ca^{2+} + 2H_2O \Leftrightarrow CaSO_4{*}2H_2O_{(s)}$ (Eq 5)

$Fe^{2+} + CaCO_{3(s)} \Leftrightarrow FeCO_{3(s)} + Ca^{2+}$ (Eq 6)

$Fe^{3+} + 3H_2O + 2CaCO_{3(s)} \Leftrightarrow Fe(OH)_{3(s)} + 2Ca^{2+} + HCO_3^- + CO_2 + H_2O$ (Eq 7)

$Fe^{3+} + 3/2Ca(OH)_{2(s)} \Leftrightarrow Fe(OH)_{3(s)} + 3/2Ca^{2+}$ (Eq 8)

$Al^{3+} + 3H_2O + 2CaCO_{3(s)} \Leftrightarrow Al(OH)_{3(s)} + 2Ca^{2+} + HCO_3^- + CO_2 + H_2O$ (Eq 9)

$Al^{3+} + 3/2Ca(OH)_{2(s)} \Leftrightarrow Al(OH)_{3(s)} + 3/2Ca^{2+}$ (Eq 10)

While the addition of alkaline materials to treat acid mine drainage is widespread in active and passive treatment plants (Morin and Hutt 1997; Kleinmann et al. 1998; Sengupta 1993), the direct addition of alkaline solids to overburden is less common worldwide. One reason is that the total amount of acidity in an overburden dump, which is required to calculate the rate of alkaline addition, is generally unknown. However, for the Garzweiler lignite mine, the amount of stored acidity in the overburden material is known (Wisotzky and Obermann 2001). Aside from the Rhineland mining area, research in alkaline addition has proceeded in northern Appalachian states (USA) and at some hard rock sites (e.g., Perry and Brady 1995; Wiram and Naumann 1996).

The pilot-scale field experiments discussed below were based on laboratory experiments in which alkaline substances were added to overburden material from the Garzweiler open pit mine (Kringel 1998). The experimental columns in which alkaline material had been added showed improved water quality compared to a reference column without added alkaline material. The pH was 3.4 in the reference column but more than 6 with added limestone or fly ash plus limestone, and dissolved iron and sulfate concentrations in the pore water of the treated columns were lower (Table 1).

The rising groundwater table will not reach the base of the limed area of the Garzweiler dump until the year 2005 at the earliest. In order to investigate the groundwater quality of a limed overburden dump earlier, and under controlled conditions, water chemistry was monitored in pilot-scale containers treated with added alkalinity (limestone, fly ash plus limestone) and compared to those in an untreated reference container.

Methods

The pilot-scale experiments were conducted with 13 metric tons of wet overburden and 2.7 m^3 of water added to each container, which together with the pore water already in the overburden resulted in a total of 3.6 m^3 of water in an average container. The ratio of overburden to water was 3.4 kg/l, which is a little lower than the "normal" value of about 4 kg/l, mainly because of the presence of filter layers of non-reactive quartz sand installed around the inlet and outlet screens. All containers had similar proportions of overburden and water, so the results are comparable. Water samples were collected from each container after coupling the inlet and outlet screens and pumping for about half an hour without atmospheric contact.

An average oxidized pyritic sulfur content of 0.036 wt % was determined by leaching all of the sulfate out of overburden samples taken when the containers were filled. The amount of alkaline substances added was based on the earlier laboratory studies (Kringel 1998). The containers were saturated with groundwater typical of the deep aquifers at the Garzweiler open pit, after being sealed against the atmosphere. The changing water chemistry was then analysed on 23 sampling dates over one year. The following parameters were measured: pH, Eh, temperature, electrical conductivity, $Fe^{2+/3+}$, Ca^{2+}, Mg^{2+}, Na^+, K^+, Al^{3+}, SO_4^{2-}, Cl^-, NO_3^-, HCO_3^-, total CO_2, alkalinity ("m-value"), alkalinity after reaction with calcite ("mH-value") and trace elements (Co, Ni, Zn, As, Al). Saturation indices (SI) for mineral phases were calculated with the computer code PHREEQC2 (Parkhurst and Appelo 1999). Results are presented for relevant reactive mineral phases, which, in addition to oxidized pyrite, include calcite ($CaCO_3$; Equation 3, 6, 7, 9), gypsum ($CaSO_4{*}2H_2O$; Equation 5), ferric iron hydroxide ($Fe(OH)_3$; Equation 7, 8), siderite ($FeCO_3$; Equation 6) and aluminium hydroxide ($Al(OH)_3$; Equation 9, 10).

Results

In the reference container, the pH was mostly between 3 and 4, reflecting the release of stored acidity into the water. Between days 15 and 110, it only increased to a value of 3.6, due to the low content of naturally occurring carbonate in the overburden. The addition of alkaline substances to the other containers immediately produced higher pH values, which reached a neutral pH of about 7 after half a year. The pilot scale field experiments thus illustrated the positive effect of adding alkaline material (Figure 1). In comparison to the laboratory column experiments (Table 1), higher pH-values were

Table 1. Selected parameters of water samples from laboratory column experiments without (Reference) and with addition of alkaline material (Kringel 1998)

	pH	SO_4^{2-}	Ca^{2+}	Mg^{2+}	K^+	$Fe^{2+/3+}$	Al^{3+}	CO_2 total
		[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]
Reference	3.4	3570	500	73	20	930	22	75
Fly ash + limestone	6.4	2120	592	205	10	95	2	970
Limestone	6.2	1710	616	51	7	53	6	760

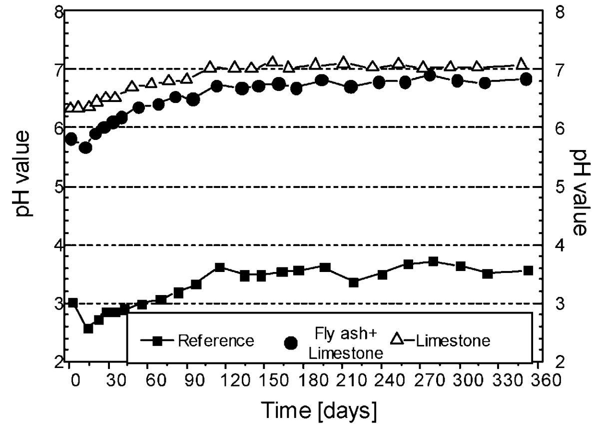

Figure 1. The pH values measured in the water of the containers without (i.e. reference) and with the addition of limestone and fly ash plus limestone. All containers were filled with the same typical sandy overburden from the Garzweiler open pit.

achieved in the alkaline containers with the addition of limestone and fly ash plus limestone.

Another goal of adding alkaline material to overburden dumps is to reduce the aggressiveness of the water against limestone (calcite). Either the difference in alkalinity before and after reaction with calcite (here called the m- and mH-values respectively, Figure 2a) or the SI-values with respect to calcite (Figure 2b) can be used as an indicator of this aggressiveness. Negative values of the differences show aggressiveness against calcite, whereas values close to zero indicate calcite/carbon dioxide equilibrium (Figure 2a). Strongly negative values observed in the water of the reference container show, in addition to low pH (Figure 1), strong aggressiveness against limestone (Figure 2). In the water of the containers with added alkaline material, the values were initially negative but reached values close to zero (Figure 2a).

The development of the calculated values of SI with respect to calcite (Figure 2b) corresponds to that of the measured alkalinity differences. Increasing pH (Figure 1) and decreasing aggressiveness (Figure 2) indicate the dissolution of calcite and/or $Ca(OH)_2$ in the containers with added alkaline substances.

In addition to neutralizing acidity, the addition of alkaline material should also cause a decreased sulfate content due to precipitation of gypsum (Equation 5), driven by the dissolution of calcium (Equation 3, 4, 6-10). Sulfate concentrations were very high in the reference container and increased during the experiment due to the slow dissolution of pyrite oxidation products (Figure 3a). In contrast, in the containers to which alkaline materials had been added, lower sulfate concentrations were measured in the water despite the same initial amount of soluble sulfate (same content of oxidized pyritic sulfur) in the solid phase. At the end of the experiment, the dissolved sulfate concentration had decreased to 1600 mg/l and 2100 mg/l in the containers with the added limestone and fly ash plus limestone, respectively, while in the reference container it was about 4000 mg/l after 80 days (Figure 3a). The sulfate concentration in the water of the container with fly ash plus limestone also decreased to 2100 mg/l at the end of the experiment (Figure 3a). Overall, the measured sulfate concentrations in the different containers are comparable to the results of the laboratory column experiments (Table 1). Hydrogeochemical calculations with the computer program PHREEQC2 (Parkhurst and Appelo 1999) show an equilibrium with gypsum (SI values ~ 0) in the water of the containers with added alkalinity (Figure 3b), while the water in the reference container is sub-saturated with respect to gypsum (SI < 0).

The laboratory experiments show that the addition of alkaline materials also caused a decrease in dissolved iron concentration in the groundwater (Table 1, Figure 4). The final iron concentration in the container with added limestone was less than 100 mg/l, which is only 8 % of the iron concentration in the water of the reference container (about 1300 mg/l after 350 days). The container with fly ash plus limestone also exhibited less dissolved iron than the reference container (Figure 4), though not as different as observed in the container with limestone only. Decreasing the dissolved iron concentration by because it can prevent a drastic pH decrease

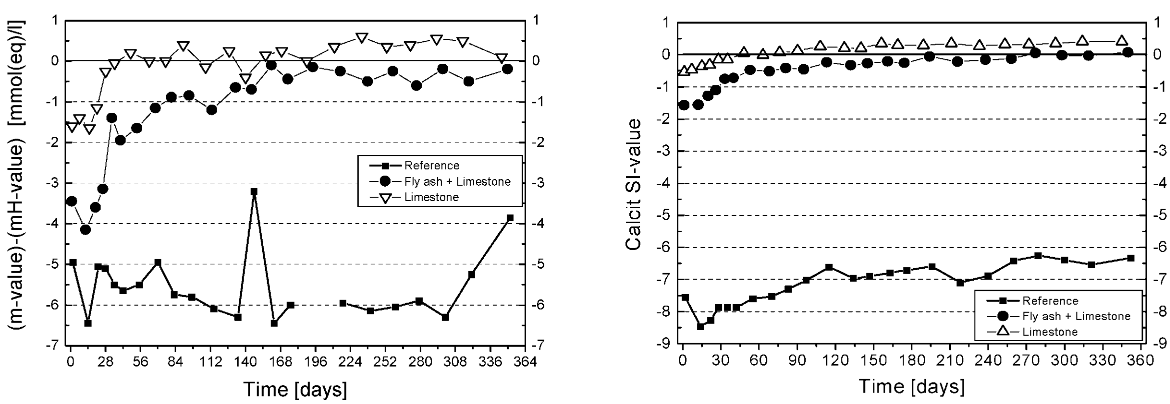

Figure 2 a) (left) Development of the measured differences of alkalinity ("m-value") and alkalinity after reaction with calcite ("mH-value") showing the aggressiveness against calcite (difference < 0) or the calcite/carbon dioxide equilibrium (difference close to 0). **b) (right)** Development of calculated saturation index values with respect to calcite (SI < 0: aggressiveness against calcite; values close to 0: calcite/carbon dioxide equilibrium)

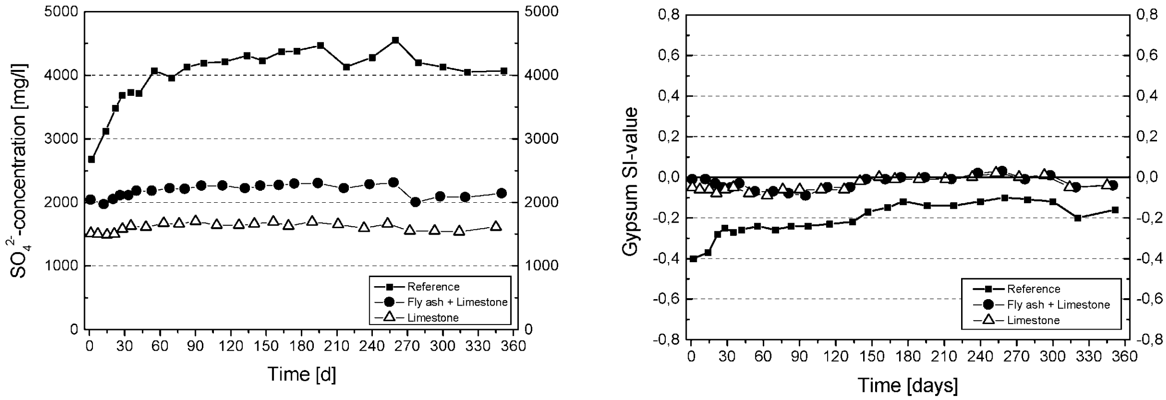

Figure 3 a) (left) Development of the measured sulfate concentrations in the water of the containers without (reference) and with alkaline addition (fly ash plus limestone, limestone). **b) (right)** Development of the calculated SI-values with respect to gypsum

following aeration. This has occurred in many residual lakes of the Lusatian and Central German lignite mining districts (e.g., Schultze et al. 1999), where it seriously limits the use of the lakes, due to pH values as low as 2.

Because the water in the reference container is always undersaturated with respect to $Fe(OH)_3$, its precipitation is not possible (Figure 5a). In contrast, all water in the containers with added alkaline substances were close to equilibrium after about 80 days (Figure 5a), with the ferric iron having precipitated, thus decreasing the dissolved iron concentration (Figure 4). The dissolved ferrous iron concentration may also have been diminished by the formation of siderite ($FeCO_3$), the SI values for which are plotted in Figure 5b. Precipitation of siderite is not possible in the reference container due to undersaturation, whereas the addition of alkaline substances leads to saturation or supersaturation with respect to siderite (Figure 5b). Supersaturation associated with siderite formation is a commonly observed phenomenon (e.g., Leuchs 1988; Morin and Cherry 1986). The proportions of iron precipitated as ferric iron hydroxide or carbonate are not yet known, but the formation of either mineral decreases the dissolved iron concentration and thereby improves water quality.

The behaviour of trace elements is illustrated by the dissolved aluminium concentration (Figure 6a). Due to pyrite oxidation and silicate weathering, the water of the reference container had a very high aluminium concentration, up to 180 mg/l. However, the

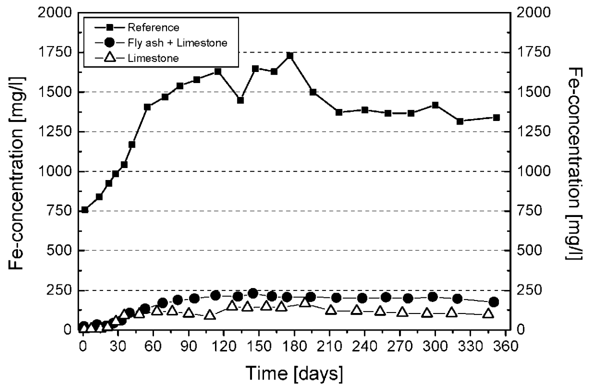

Figure 4. Iron concentrations measured in the water of the containers without (reference) and with alkaline addition (fly ash plus limestone, limestone)

increased pH due to the addition of alkaline substances caused low aluminium concentrations in the limestone and fly ash containers. Saturation index values close to equilibrium indicate the precipitation of $Al(OH)_3$ (Figure 6b) in the containers with added alkaline substances, whereas sub-saturation in the reference container prevented its precipitation (Figure 6b). Similarly, concentrations of other trace elements (mainly Co, Ni, Zn, As,) decreased with the addition of alkaline substances, compared to the high values in the reference container (Table 2).

In general, the addition of crushed limestone is preferable to the mixture of fly ash plus limestone, because of lower concentrations of Mg^{2+} (Table 1) and SO_4^{2-} (Figure 3a), and the possibility of environmentally unacceptable alkaline pH values caused by fly ash.

Table 2. Concentrations of some trace elements in the water of the containers after a reaction time of about 350 days

	Reference	Limestone	Fly ash + Limestone
Ni [µg/l]	1185	17	4
Co [µg/l]	8.2	0.6	< 0.5
Zn [µg/l]	4700	422	458
As [µg/l]	556	5.5	6.7

When acid mine water is treated in anoxic limestone drains, a reduction in the effectiveness of the limestone gravel is often observed (Kleinmann et al. 1998; Watzlaf et al. 2000) because of the formation of ferric and Al precipitates on the surface of the limestone. To avoid this problem, the grain size selected for the added limestone was smaller than 1 mm. No indication of a reduction of the alkaline effectiveness was observed in the containers within the experimental period.

Because of the positive results of the column (Table 1) and pilot-scale experiments, one part of the Garzweiler overburden dump has been treated with limestone since 1998. In 1999, about 25 million metric tons of overburden were treated with limestone there. For the future lignite mine, Garzweiler II, which will be active from 2005 until 2045, a total addition of about 6.7 million metric tons of limestone addition is planned (Kringel 1998).

Conclusion

The addition of alkaline substances (limestone or a mixture of fly ash and limestone) to acidic overburden considerably improved water quality in both laboratory column and pilot-scale field experiments, resulting in decreased sulfate, iron, and trace

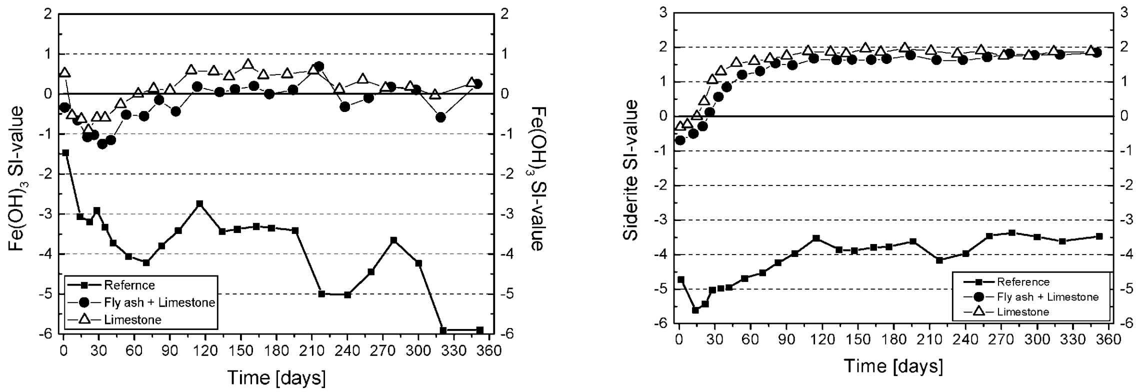

Figure 5 a) (left) Development of the calculated SI-values with respect to iron hydroxide ($Fe(OH)_3$) in the water of the containers without (reference) and with alkaline addition (fly ash plus limestone, limestone). **b) (right)** Development of the calculated SI-values with respect to siderite ($FeCO_3$)

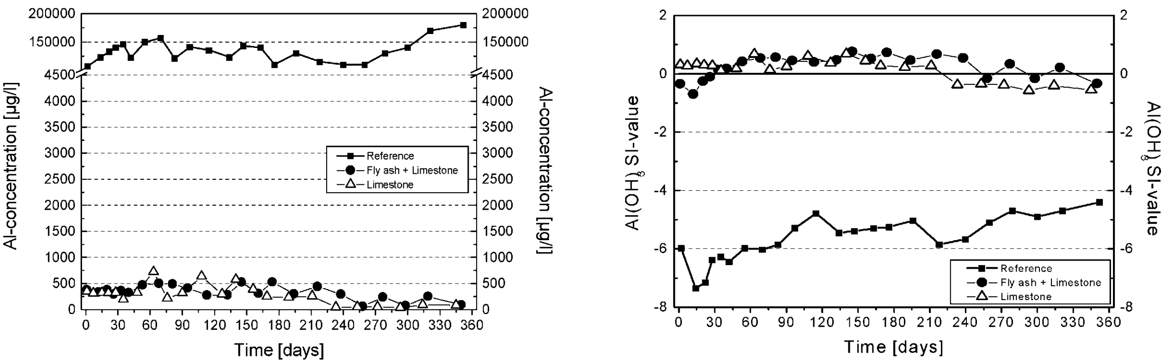

Figure 6 a) (left) Development of the measured aluminium concentrations in the water of the containers without (reference) and with alkaline addition (fly ash+limestone, limestone). **b) (right)** Development of the calculated SI-values with respect to $Al(OH)_3$

elements, and in increased pH. A comparable improvement of groundwater quality in sandy overburden dumps due to the addition of crushed limestone is expected, and, so far, limestone has been added to one part of the overburden dump of the Rheinbraun Garzweiler lignite mine in Germany.

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