

Dissolution of Various Basic Substances

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Abstract Neutralisation of Acid Mine Drainage requires equivalent amount of basic substance. Besides known products, many current projects are evaluating industrial byproducts from i.e. steel, lime/cement or power plants: Slag, lime kiln dust and ashes of different chemical and physical properties. Besides potential neutralisation capacity, which is widely examined, dissolution kinetics of mineral basic materials is getting important, as residence times of concerned processes. Within the presented communication dissolution kinetics and neutralisation potentials of various basic substances will be presented and put into economical context of industrial application.

Key Words AMD, steel slag, lime, limestone, neutralisation potential, dissolution kinetics

Introduction

Costs for the remediation of former mining sites are usually very high. Especially the treatment of AMD is cost intensive because the problem is present for decades and requires a constant make up of basic substances to neutralise the acidic water. Disregarding if active or passive systems are used to deal with this problem, the needed basicity contributes to most to the overall costs. Accordingly, efforts are undertaken to substitute commonly used limestone with other materials like steel slags (Kruse *et al.* 2010), fly ashes and portland cement (Gitari *et al.* 2010), recycled concrete (Navratil *et al.* 2010) and cement kiln dust (Mackie *et al.* 2010) in order to achieve cost reductions. However, residuals might not always be the best choice in terms of overall cost optimisation: First, residuals usually contain a lower amount of free basicity than standard products. By this, additional material that can not be used for the neutralisation has to be transported. Second, the dissolution of the basicity in residuals is rather slow. This causing the need for larger treatment installations compared to the amount of the water that shall be treated.

Theoretical Background

Description of Dissolution

Diffusion or chemical reaction can be rate determining for the dissolution kinetics of a soluble salt. In case of $\text{Ca}(\text{OH})_2$ the diffusion of Ca from the surface of the particle into the solution is rate determining (Schüppel 2009) and can be calculated according to Fick's first law by

$$\frac{dn}{dt} = -D \cdot A \cdot \left(\frac{dc}{dr} \right) \quad (1)$$

dn/dt is the mole flow, D the diffusion constant, A the surface and dc/dr the change in concentration over the diffusion layer. Schüppel was

able to show via modelling work that the dissolution kinetics of different $\text{Ca}(\text{OH})_2$ products is only a function of particle size distribution and therefore of the outer surface area. Consequently, higher outer surface cause a faster dissolution rate. Accordingly, fine calcium hydroxide powders are able to dissolve very quickly.

Describing the dissolution of carbonates, like CaCO_3 , is harder, because H^+ ions are diffusing to the surface of the carbonate and react with the CO_3^{2-} to HCO_3^- . This hydrogen carbonate is able to react with other H^+ to H_2CO_3 that dissociates into H_2O and CO_2 . By this mechanism, the concentration of the ions from the dissolved salt changes considerably with the outer adjusted pH-value. Accordingly, the dissolution rate of carbonates depends strongly on the pH-value (see Figure 1).

Considering residues like lime kiln dust or steel slag the complicity of the system is even increased further: Many phases can be present at once (e.g. CaO , $\text{Ca}(\text{OH})_2$, CaCO_3 , NaO , Fe and Al phases) and interacting with each other during the dissolution causing, for example, re-crystallisations. Consequently, the empirical observation of the dissolu-

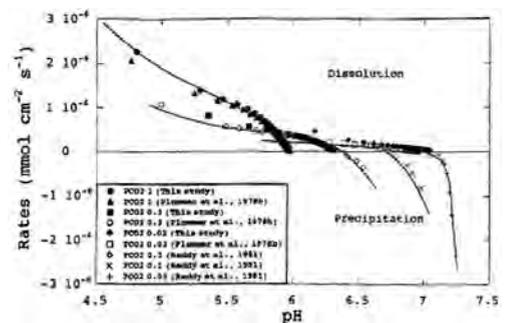


Figure 1 Dissolution rates of CaCO_3 at different pH-Values. Figure taken from Arakaki & Mucci (1995).

tion of such complex systems might be the best possibility to study the dissolution kinetics as well as the neutralisation potential.

Neutralisation Potential

In the scope of this work two different neutralisation potentials (NP) are used: First the utilisable NP, NP_{Util}, which is defined as the basicity that is dissolved within 30 minutes under a constant pH-value of 6. And, second, the maximal NP that is derived from the chemical composition by

$$NP_{Max} = \left(\frac{[CaO]}{56} + \frac{[MgO]}{40} \right) \cdot 2 \cdot 10 \quad (2)$$

The unit of both NPs is mol_{OH⁻}/kg. NP_{Max} overestimates the NP because possible phases associated with Ca like 3 CaO·SiO₂, are not taken into account and subtracted from the NP.

Investigations

Experimental Setup

Titration at a constant pH-value of 6.0 were carried out. This pH-level was chosen because most of the dissolved metals (e.g. Fe or Al) in AMD are precipitated and the run-off water is often classified as non hazardous at this pH. A “Dosimat 805” produced by “Metrohm Ionenanalytik AG” was used for the investigations. 0.5 M H₂SO₄ solution was used to titrate a 100 ml slurry containing 0.5 g of the according basic substance which was added to the water right at the start of the measurement. The volume of the added acid was recorded continuously. Titrations were done for 30 minutes.

The chemical composition was determined by X-ray fluorescence with a “Siemens MRS 404”

Table 1 Chemical composition and particle size distribution of the investigated products: hydrate lime (HL), limestone (LS-c, -f), fly ash (FA) and hydrated dolime (HD)

	HL	LS-c	LS-f	FA	HD
CaO	72.8	54.69	50.43	49.57	45.01
MgO	0.74	0.50	0.45	1.91	31.81
SiO₂	3.3	0.85	6.36	10.6	1.65
SO₃	0.161	0.047	0.09	25.65	0.37
Fe₂O₃	0.33	0.11	0.39	4.00	0.93
Al₂O₃	0.25	0.21	1.36	4.95	0.78
Mn₂O₃	0.03	0.04	0.04	0.06	0.21
K₂O	0.08	0.06	0.21	0.15	0.02
Cl	n.a.	n.a.	0	0.07	0.08
CO₂	2.36	43.48 ¹	40.08 ¹	n.a.	1.47
LoI	22.11	n.a.	40.53	3.02	19.04
d₁₀ [µm]	1.1	1.5	0.8	2.5	1.5
d₅₀ [µm]	6.7	8.9	2.6	20.3	7.4
d₉₀ [µm]	56.6	28.4	7.6	97.7	27.5
d₀₇ [µm]	82.5	47.8	12.1	135.1	51.5
d₁₀₀ [µm]	123.0	103.0	30.0	206.0	103.0

¹ Value was calculated based on the chemical composition and the LoI.

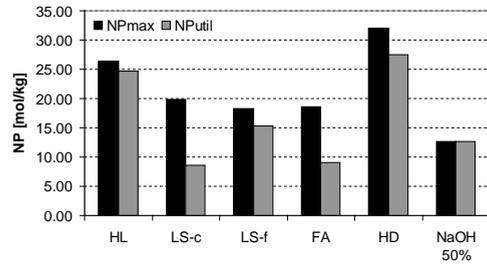


Figure 2 NP_{Max} and NP_{Util} of the investigated products after 30 minutes at a pH-value of 6.

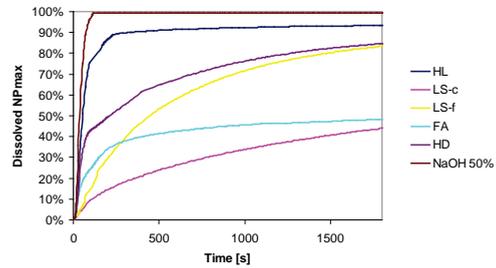


Figure 3 Dissolved maximal NP versus time at a pH-value of 6. The relative ranking after 30 minutes is NaOH > HL > HD > LS-f > FA > LS-c

while the particle size distribution was measured by laser light diffraction with a “Sympatec Helos”.

Basic Substances

Five different products had been selected for the investigations: hydrate lime (HL), powdered limestone – coarse (LS-c) and fine grained (LS-f), fly ash (FA) and hydrated dolime (HD). A 50wt.% solution of caustic soda produced by Merck was used as reference. The chemical composition and the particle size distributions of the substances can be seen in Table 1.

Results and Discussion

Results

Figure 2 illustrates the maximal and utilised NP. It can be seen, that HL had the highest utilisation degree besides the reference of the 50% caustic soda solution.

HD had the highest overall NP. This is a direct result of the low molar mass of Mg(OH)₂. It is interesting to note that the utilisation degree between coarse and fine limestone powder varies nearly by a factor of two. This effect is believed to be caused by the much improved dissolution rate in the case of the LS-f due to the significant higher outer surface area.

The dissolution kinetics of the products are illustrated in Figure 3. LS-c performed poorest while HL performed best.

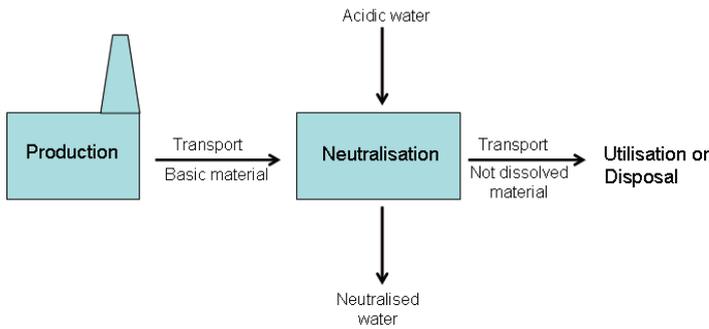


Figure 4 Principle flow scheme of the neutralisation of acidic water with a basic material.

HD, LS-f and LS-c were still dissolving with notable rates while FA, even though it had a very high initial dissolving rate, seem to have reached a steady state at the end of the titration.

In case of FA a foully smell (most likely H_2S) was recognised during the titration. Therefore technical applications of this residue might be limited due to the hazardous nature of high H_2S concentrations in the atmosphere.

Technical Relevance

The performance of technical neutralisation installations is directly linked with the dissolution kinetics of the basic substances. In case of small installation and high water throughput high dissolution speeds are mandatory to precisely adjust the pH-value at the outlet of the reactor and to prevent any acidic water from leaving the system and any after dissolution of particles that would cause undesired high pH values in the treated run-off waters. Consequently, HL should be used for those applications.

In case of large, passive systems limestone should be used. By this, a pH-shift to too basic waters could be prohibited. The throughput in relation to the neutralisation interior (τ -space time) of the reactor determines the fines of the product.

$$\tau = \frac{n_{\text{Reactor}}^{\text{OH}^-}}{n_{\text{Reactor}}^{\text{H}^+}} \quad (3)$$

$n_{\text{Reactor}}^{\text{OH}^-}$ are the moles of basicity that are in the reactor while $n_{\text{Reactor}}^{\text{H}^+}$ is the flow of acidity into the reactor.

High space times allow a slow dissolutions kinetic and therefore the use of a coarse product while low space times would require a fine limestone with a fast dissolution kinetic.

Another critical point during the neutralisation of AMD are incrustations on the particle surfaces that prohibit a further dissolution of the basicity. Consequently, counter flow reactor in that the acidic water enters the reactor at the bottom and leaves it at the top are preferable. By this, precipitates could be washed away enabling a con-

stantly fresh surface area. By technical optimisation optima between reactor height, dissolution rate and water flow have to be derived.

Economical Considerations

The total costs for neutralisation of acidic waters are composed of different elements: Production and transport of alkaline Material, neutralisation process and the handling of residual products. In this comparison, only the material related costs are taken into account: First of all a alkaline material is needed: Commercial products are available at market prices; residuals or byproducts are typically between those commercial products or even for free, depending on their alternative applications. Attention needs to be paid for their environmental impact and their dissolution kinetics as discussed before. Fly ashes from paper incinerations, for example, have a market price in the range of 10–15 €/t. After the production the material has to be transported. These costs are assumed in the order of magnitude of 8 €/t (100 km). At the neutralisation site, the basic material has to be handled, e.g. it has to be stored in silos and transported. The costs for the product handling are set in this calculation to 10 €/t for all products. Especially in case of residuals a rather high amount of solid will not dissolve during the neutralisation. This causes the need for further utilisation or disposal of the not dissolved basic solids. However, due to the changing composition and contamination in most cases the created final residue need to be disposed. Consequently, dumping costs were also set constant for all products to 100 €/t_{Dumped}. Figure 4 illustrates the principle flow scheme for the costs of the neutralisation of acidic water.

The product costs were estimated to 100 €/t for HL, 25 €/t for LS-c, 35 €/t for LS-f, 15 €/t for FA and 100 €/t for HD. Figure 5 illustrates the specific costs for basicity versus the distance of transportation.

It can be seen that HL, LS-f and HD have nearly the same specific overall costs for one mole of OH^- while LS-f is cheaper for distances below

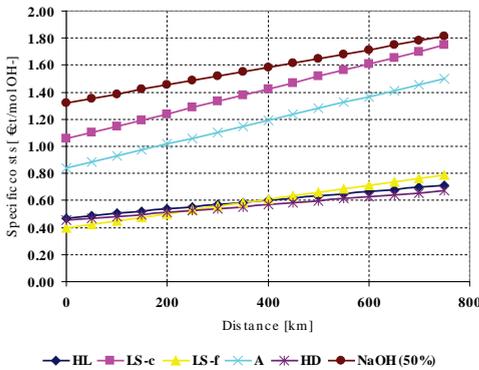


Figure 5 Specific costs for basicity versus the distance of transportation.

200 km and HD becomes less expansive for distances above 200 km. The residue A is roughly twice as expansive as HL, LS-f and HD if it hasn't to be transported. In case of long distance transportations the relative gap becomes even bigger.

Conclusion

To find the economic and environmental appropriate solution to treat AMD, it is not sufficient to look only for the theoretical neutralisation potential of basic substance to be used. Dissolution kinetics need to be considered in the complex interdependent system of chosen treatment technology, availability of basic substances and connected transports and eventual disposal of generated substances.

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