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A potential process for the neutralisation of industrial waste acids by reaction with olivine

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Abstract

Industrial waste acids such as sulphuric and hydrochloric acid are produced in large quantities. This note deals mainly with waste sulphuric acid, although similar results have been obtained with hydrochloric acid. A method is described by which these acids can be neutralised using crushed olivine rock. This process produces silica. The heavy metals present can be precipitated from the resulting solution. The remaining clean magnesium-sulphate solution can be dumped at sea without adverse environmental consequences. The process has been patented (Dutch patent PCT NL 85/00026), and is being further developed in cooperation with Dutch industries. Silica, one of the major products of the process has been tested as an additive to concrete. An addition of between 5 and 10% silica greatly decreases the permeability of concrete, thereby increasing the resistance of concrete constructions under chemically aggressive conditions.

Introduction

Many industrial processes use or produce acids. Afterwards, the diluted and contaminated waste acids must be removed. The three options to achieve this are dumping, recycling or neutralisation. Dumping usually takes place by disposal in rivers or at sea, although subsurface waste disposal can also be envisaged (Visser & Weber, 1972).

As the environmental constraints on dumping are tightened, industries are being forced to look for the two alternative solutions. Reprocessing waste acids for re-use is often expensive and thus the normal choice is neutralisation. A widely available and cheap neutralising agent is limestone, but unfortunately the end-product is a contaminated gypsum. As the marketing outlook, even for relatively clean gypsum is rather bleak (Weterings, 1980) such a contaminated gypsum poses a serious disposal problem. An alternative process, circumventing the problems mentioned above, is neutralisation by reactive silicates.

Neutralisation of acids in nature

Production of acids is not confined to industry. Several natural processes produce large quantities of acids. The yearly production of sulphuric-acid by volcanoes has been estimated at $15.3*10^6$ tonnes (Stoiber & Williams, 1983). In addition volcanoes produce large quantities of hydrochloric acid and CO_2. Another important source of sulphuric-acid is from the oxidation of sulphides, in particular pyrite, during weathering. A conservative estimate for this contribution is $20*10^6$ tonnes/year, taking into account average rates of weathering and mean concentration of sulphur in rocks. It is clear that all

of these acids are neutralised in the weathering cycle. Although chemical weathering proceeds fastest in carbonate rocks, these processes constitute only intermediate steps in a larger geochemical cycle, as their calcium and magnesium must ultimately derive from the weathering of silicate rocks.

Silicate rocks thus provide the ultimate buffer against acidification. However, certain silicates weather much faster than others. Amongst the common silicates, quartz, potassium-feldspar and muscovite survive for a long time in most weathering regimes, whereas pyroxenes, amphiboles and particularly olivine disappear rather rapidly. This is certainly one of the reasons why acid rain has a more devastating effect on forests on sandy soils than those whose chemical regime is controlled by volcanic rocks or carbonates.

It seems logical, therefore, to examine the possibility of neutralising industrial acids with reactive silicate rocks, thereby imitating natural weathering. By selecting the most reactive of the common silicates, using crushed instead of solid rock and operating with concentrated acids at slightly elevated temperatures compared to natural weathering, the potential process may operate at such a fast rate, that it becomes a technologically interesting option.

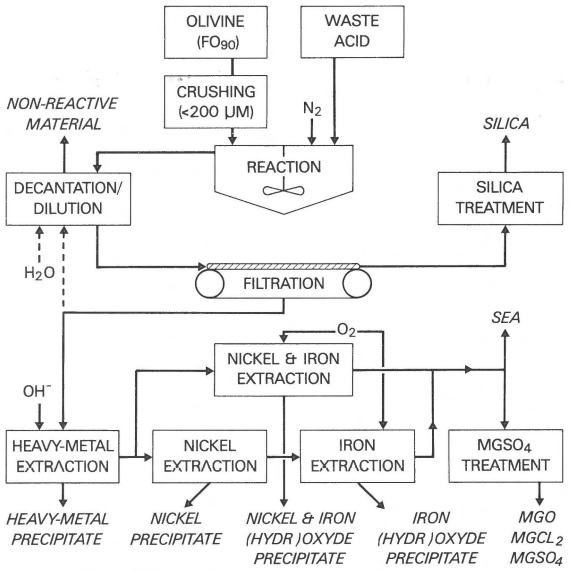

Fig. 1. Schematic flow-sheet of the olivine process.

The olivine process

Fig. 1 shows the proposed steps of the process. Crushed olivine rock is reacted with waste acid. As the reaction is exothermal it sustains itself, after heating to initiate the reaction. The olivine used in the experiments has a composition as given in Table 1, and a mineral formula that can be approximately written as $(Mg_{1.85}Fe_{0.14}Ni_{0.01})SiO_4$.

Table 1. Chemical composition of olivine (forsterite) and mineralogical composition of olivine rock from Norway.

Analysis of forsterite				Associated minerals in olivine rock	
SiO_2	41.00	Si	0.999	forsterite	94%
Al_2O_3	–	Al	–	talc	2.7%
Cr_2O_3	–	Cr	–	intergrown minerals*	2.1%
TiO_2	–	Ti	–	pyroxene	0.9%
FeO	6.99	Fe	.143	Cr-spinel	0.3%
MnO	.11	Mn	.002		
MgO	50.82	Mg	1.845		
NiO	.64	Ni	.013		
CaO	.06	Ca	–		
Na_2O	–	Na	–		
Total	99.58		3.001		

* = mainly olivine with spinel (fraction <250 u and Frantz magnetic separation, analysis Guinier-Wolff camera).

This olivine originates from Norway but there are many other olivine producers, e.g. Spain. Olivine-rich rock is available in large quantities and with an essentially unlimited supply. With the olivine from Norway, which is reasonably representative of other occurrences, the reaction with sulphuric acid can be written as

$$((Mg_{1.85}Fe_{0.14}Ni_{0.01})SiO_4 + 4H^+ + 2SO_4^{2-} \rightarrow 1.85Mg^{2+} + 0.14Fe^{2+} + 0.01Ni^{2+} + 2SO_4^{2-} + H_4SiO_4$$

The silicic-acid polymerises rapidly, during which small spherules of silica are formed, which have a tendency to form larger aggregates. By suitable choice of the process parameters the size of these spherules can be regulated in such a way that the silica can be conveniently filtered and washed. After this initial step there is a choice; the dissolved nickel can either be extracted while the pH is still rather low (e.g. by ion exchange) or one can wait with the precipitation of nickel until the pH is much higher. The waste acid for which the process has been primarily developed is produced by a titanium-dioxide plant and it contains other metal contaminants, notably titanium, vanadium and chromium.

After filtration of the silica at low pH (1–2), the pH is raised and chromium and vanadium are precipitated. Following this, the system is oxidised by bubbling air through the system. As a result iron precipitates, depending on the pH at which the oxidation is carried out, as an amorphous iron hydroxide (very effective as a scavenger for any remaining contaminant, but difficult to filtrate) or as an ironoxide (permitting faster filtration). If nickel has not been extracted earlier at low pH it will almost quantitatively co-precipitate together with the iron during the oxidation step.

Finally, a clean, concentrated magnesium-sulphate solution will remain, which becomes supersaturated at room temperature. To prevent the precipitation of hydrated magnesium-sulphates, all filtration steps mentioned earlier need to be carried out at an elevated temperature (in the order of 100° C), as otherwise the whole system becomes clogged with prematurely precipitated sulphate. There should be no environmental objections against the dumping of a clean magnesium-sulphate solution into the sea (which is after all a mixture of water, NaCl and Mg-sulphate!). The best philosophy for a process that aims at solving an environmental problem is, however, that everything is done to ensure a maximum recovery of by-products, including magnesium-sulphate.

The last by-product is formed by the insoluble minerals of the olivine rock, mainly pyroxenes and some chromite. Separation of these residual minerals from the silica is quite simple but unless the small quantities of chromite warrant such a separation step, this residual material can be dumped, as it contains no leachable harmful substances. Similar results have been obtained with hydrochloric acid although the silica here shows somewhat different properties.

Factors affecting potential application

The economy of the process depends on a number of factors. The availability of good quality of olivine is no problem. Filterability of the silica and of iron (hydr-)oxide were problems in the early stages of the research but these have been satisfactorily resolved. The major uncertain factor is the price and the size of the market for the silica, which is obtained as a white fluffy powder. Experiments using the silica as an additive (5–10%) to concrete have shown that the mechanical strength of the concrete is improved, but more important is that the permeability is greatly decreased. It is expected that for concrete constructions that must withstand chemically aggressive conditions such silica will find a valuable application. For the moment the magnesium-sulphate remains a problem, as environmental legislation restricts the dumping of large quantities of sulphate, irrespective of its form. However, there can be no realistic objection against the dumping of clean magnesium-sulphate in the sea for reasons discussed earlier.

The estimated nett costs of the olivine process for a plant treating 300.000 ton of 20% waste sulphuric acid would come at 10 to 20 million Dfl. on an annual basis, which compares favourably with

the other options mentioned in the introduction. A summary of the estimated costs and benefits is presented in Table 2.

A significant advantage of the proposed process is that the industrial acids will be neutralised at their source and that the residual solutions are stripped of their contaminants, before being released to the environment. In addition the process uses cheap raw materials, needs little energy, and produces some economically interesting by-products. It is therefore considered to be a potentially attractive alternative to existing systems for the elimination of industrial waste acids.

Table 2. Summary of estimated costs and benefits on an annual basis of the olivine process. Note that in this calculation it is assumed that the heavy metal residue is disposed as chemical waste. If vanadium and/or nickel are extracted, the nett costs of the process might be lower.

Variable costs (olivine raw material, neutralization agents, energy costs, disposal costs of residues)	Dfl 24	
Fixed costs (personnel, maintenance and overhead)	Dfl 6.5	
Depreciation (15% of capital investment)	Dfl 10	
		+
Total expenditure	Dfl 40.5	
Total benefits (Depending on the price that can be obtained for the silica, excluding possible benefits from vanadium and/or nickel extraction and uses of $MgSO_4$)	Dfl 20–30	
		−
Nett cost	Dfl 10–20 × 10^6	

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