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THE OLIVINE PROCESS - WASTE ACID NEUTRALIZATION BY REACTION WITH A MAGNESIUM SILICATE.

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ABSTRACT

An alternative process for the neutralization of inorganic waste acids is presented. The process uses the most reactive silicate mineral available, olivine, and essentially imitates the natural process of acid neutralization (chemical weathering). The process is particularly useful for the neutralization of fairly concentrated acids. With concentrated acids the reaction sustains itself, as it is exothermic. Neutralization of acids takes only a couple of hours, which makes the process a technologically interesting option. However, also with less concentrated acids the potential neutralizing capacity of crushed olivine is remarkable, provided the factor time is of limited importance. Understanding of reaction kinetics of natural processes has reached a point at which reaction mechanisms can be quantitatively described; this permits the prediction and solution of problems associated with acid mine drainage.

INTRODUCTION

The waste acid problem.

Many (mining) industries use large quantities of acids. Afterwards the diluted and usually contaminated waste acids must be removed. At the moment three options exist to achieve this; dumping (either at land or in sea), acid recycling and neutralization. Dumping is nowadays considered to be an environmentally poor alternative and recycling is usually very expensive (high costs for energy and dumping of solids). Neutralization may therefore be a suitable alternative provided the end- or by-products resulting from this type of process are of a relatively high purity and consequently may find an application. This is for instance not the case when sulphuric acids are neutralized with carbonate rock (lime); the gypsum resulting from this reaction can hardly be applied in most industrialized countries [1].

Alternative chemicals for acid-neutralization are available, but in most cases prices are prohibitive; therefore they only find limited use. At Utrecht University, the Netherlands, a process has been developed, which uses crushed olivine, a widely available and cheap reactive magnesium-silicate mineral. The process is particularly useful for the neutralization of inorganic waste acids, typically containing iron and other heavy metals. It is an alternative for neutralization with base or lime. The process is patented by the University [2]. Detailed description of the process has been presented elsewere [3,4,5].

Neutralisation of acids in nature - weathering index.

Production of acids is not confined to industry. A number of natural processes also produce large quantities of acids. For instance, the yearly production of sulphuric-acid by volcanoes has been estimated at $15.3 * 10^6$ tonnes per year [6]. In addition, volcanoes produce large quantities of hydrochloric acid and CO_2. Another major source of sulphuric acid is from oxidation of sulphides (pyrite) during weathering. Taking into account average rates of weathering and mean concentration of sulphur in rocks, a conservative estimate for this contribution is $20 * 10^6$ tonnes per year. Acids produced in this way are neutralized in the weathering cycle. Of course, chemical weathering proceeds fastest in carbonate rocks. This process constitutes, however, only an intermediate step in a larger geochemical cycle, as their calcium and magnesium derive from the weathering of silicate rocks. Silicate rocks therefore provide the ultimate buffer against acidification.

Geochemists have classified minerals according to their persistence at the surface of the earth. One of the earliest modern workers in this field was Goldich [7], who noted the similarity between the mineral sequence in order of increasing surface stability and the mineral stability for crystallization in a silicate melt, predicted by Bowen [8]. Since 1938, a number of similar classifications has been presented in the literature [e.g. overview in 8]. These classifications were all based on different methods (for instance bonding schemes, linkage of silica tetrahedra), but they all resulted in similar classification sequences [table 1].
Efforts to truly quantify the weathering indexes have only been carried out recently, and suffer from the fact that many authors are involved, making a normalised procedure difficult. One of the most recent efforts has been carried out by Lasaga [10]; he derived a sequence of minerals, ordered by a decreasing rate of silica release: nepheline > anorthite > diopside/enstatite > albite > K-feldspar > forsterite > muscovite > quartz. This sequence was, except for forsterite, in complete accord with the weathering sequence of Goldich. Later, these data were corrected with new values for forsteritic olivine [fig. 1 and ref.11], and came into agreement with field observations. In fig.1 the reaction rates of a number of magnesium silicates are compared.

THE OLIVINE PROCESS

The reaction.

Essentially, the process simulates in a speeded up way, the acid-neutralization process in nature, and it is therefore less likely to disturb natural geochemical cycles. Olivine is a mineral, which is widely available in Western Europe. Total yearly production is about 1.5 million tons, 60 % of which is produced by the world largest olivine mines, situated in South Norway [12]. Most of the production is exported as a slag conditioner to the iron- en steelmaking industry in Europe. The olivine used in the experiments has a chemical composition as given in table 2. The mineralogical composition of olivine rock (dunite) is also presented in this table.

Table 1.
Persistence order of minerals, in order of increasing weathering stability [adapted from 9].

Forsterite (olivine)
Actinolite
Diopside
Sillimanite
Augite
Hornblende
Talc
K-feldspar
Magnetite
Ilmenite
Biotite
Muscovite
Quartz

Table 2.
Chemical and mineralogical composition of forsterite and olivine rock.. The olivine originates from Norway.
* Maximum value (usually 0.25 %).

SiO_2	41.00 %
FeO	7.00
MnO	0.11
MgO	50.82
NiO	0.60 *
CaO	0.06
Total	99.59

Forsterite	92-95 %
Talc/serpentine	1-3 %
Pyroxene	1-2 %
Oxides	0.3-1 %
Intergrown minerals	1-3 %

At Utrecht University, the process has been developed on a large lab scale; the reaction can be carried out continuously. The process is tested with waste acid from the titanium pigment industry; kinetic studies have been carried out with clean sulphuric - and hydrochloric acids. A process flowsheet is presented in fig. 2. The reaction of olivine with sulphuric acid is exothermic; the reaction enthalpy is 351.3 KJ mole^{-1}. Activation energy is 30 +_ 2 KJ mole^{-1} [11].

In the process, the olivine rock is first crushed to a grainsize < 250 micron [fig. 2 A]. With the olivine used in the experiments and sulfuric acid the reaction can be written as:

$$(Mg_{1.85}Fe_{0.15})SiO_4 + 4H^+ + 2SO_4^{2-} \longrightarrow$$

$$1.85Mg^{2+} + 0.15Fe^{2+} + 2SO_4^{2-} + H_4SiO_4$$
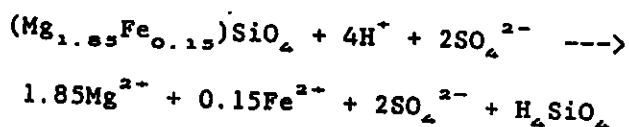
In the process a series of continuously stirred tanks are used for the reaction. Backmixing facilities are optional and provide an even better conversion [fig. 2 B]. With a suitable choice of process parameters (temperature, olivine grainsize, acid strength), neutralization takes place within three to four hours; the pH reached is about 1.5 to 2.5. Kinetic data of experiments carried out with different acid strengths, different temperatures and different grainsizes are presented in fig. 3, 4 and 5. The reaction is carried out with a 5% excess of olivine, because the commercially available olivine-rock consists only for 92-95 % of forsterite (table 2).

If a more than stoichiometric amount of olivine is used, the pH reached may be higher (up to pH 3.5), provided the waste acid contains a limited amount of iron. High amounts of ferric iron may act as a buffer; in those cases it is necessary to prevent oxidation. Addition of strong complexing ligands may in some cases also increase the reaction rate.

Filtration of the silica.

The silicic acid during the reaction rapidly polymerizes to an amorphous silica (at concentrations > 100 ppm Si) and is finally filtered from solution.

$$H_4SiO_4 \quad ---> \quad SiO_2 + 2H_2O$$
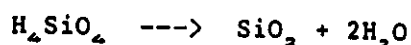
The total amount of silica formed in the reaction depends solely on the acid strength. With relatively low acid strengths the reaction will only produce small amounts of silica which will not have to be removed from solution. In terms of the required installation this means that no capital investment for filtration units is needed; on the other hand, the revenues from silica sales will also be absent.

In more concentrated acids, the speed of filtration depends on the particle size of the silica, which consists of aggregates of separate particles, ranging in size between 20 and 80 nm and on the higher viscosity of the magnesium-sulphate (or chloride) solution. Plate 1 shows an EM photo of these silica particles and plate 2 of the larger aggregates. Heat-aging of the silica results in a marked increase in filtration speed, as is indicated in fig. 6. The heat-aging process is schematically presented in fig.7; the aging process is extensively treated by Iler [13]. High viscosities of the reaction mixture may be avoided by diluting the mixture prior to filtration [fig.2C ; fig. 6].

Application of silica.

Non-purified silica is usable as an additive to concrete. Addition of a small amount of silica increases the strength and decreases the permeability of the concrete [14]. At the moment, special interest is put in the development of alkali-silica-fly ash(PFA)-sand mixtures, producing a cement-like material with high strength and a good acid resistance [15,16].
In a purified form the silica particles are potentially usable as a high quality additive to rubber, plastics or paint. To obtain a purified silica, it is essential to remove the residual non-reactive minerals (table 2). For this reason a hydrocyclone is added to the process [fig. 2 D]. The purified silica contains more than 99 % SiO_2, making it an interesting and potentially valuable chemical. Other comparable micro-silicas cost over $800,- /tonne [17].

Removal of heavy metals, iron and magnesium.

At the pH reached upon neutralization most metal-ions remain in solution so the next step in the process may be a selective extraction according to known methods. It is stressed here that each typical waste stream needs an individual treatment, depending on its composition. The example discussed here deals with waste acids from the titanium pigment industry; these acids typically contain aluminium, iron, chromium, vanadium and manganese. Total yearly production in Western Europe is 1.2 million tonnes (expressed as 100 % sulphuric acid !) which is dumped in or near sea. Removal of heavy metals from chloride waste streams is usually more effective as most elements form strong chloride-complexes [18].

The waste acids produced by the titanium pigment industry contain high amounts of iron. In order to minimize the production of a large quantity of mixed hydroxides coprecipitation of iron and heavy metals should preferably be avoided. The most effective way to accomplish this is to prevent the iron to oxidize. Therefore the reaction should either be carried out in an inert atmosphere (prevention technique) or the iron should be reduced by using a more aggressive reductant [e.g.19]. Consequence is that the iron precipitates only at a pH of 6 instead of 2-3. This opens the possibility to precipitate and filtrate a number of heavy metals at a pH of 4 [fig.2 G]. Precipitation of the heavy metals is accomplished by adding a base.

Next, the remaining iron is oxidized and precipitated as magnetite, using a method similar to the Japanese Ferrite process [20,21,22] [fig.2 H]. An advantage of this method is that the iron forms crystalline magnetite particles, which is favourable in the solid-liquid separation process. The small amounts of nickel from the olivine coprecipitate with the magnetite [23]. The iron oxide is sold to the steelmaking industry.

It is stressed here that only the use of magnesium-based neutralization compounds offers the possibility of separating heavy metals and iron, due to the very high solubility of magnesium-compounds compared to calcium-compounds.

The finally remaining magnesium salt solution may either be dumped at sea (seawater already contains 0.3 % magnesiumsulphate [24]) or, if large quantities of acid have to be treated, converted to caustic magnesia.

APPLICATION AND PROCESS ECONOMICS.

Example from the titanium pigment industry.

As mentioned before, the process has been tested with waste acids from the titanium pigment industry. In cooperation with Dutch industries a feasibility study has been made to neutralize 30 M^3/hour [4]; on an annual basis 70.000 tonnes of hydrosulphuric acid (recalculated to 100% acid) had to be neutralized, which required about 60.000 tonnes of olivine and produces 22.000 tonnes of micro-silica, 3000 tonnes of heavy-metals and 12.000 tonnes of iron-oxide.

Conclusion was that the process is technically feasable, requiring a capital investment of about 20-30 million dollar. At the moment of study, it was still unsertain if a break-even could be achieved, due to uncertainties over the marketing of the silica. Still, the process compares favourably with respect to other alternatives. Main reason is that only a limited amount of heavy metal residue is created, because iron is removed separately; as a consequence, the precipitate contained an interesting high vanadium concentration (10-15 % V_2O_5). Vanadium is an element of strategic importance. Some factors of general economic importance will now be discussed briefly. It will be clear that it is not possible to present a detailed economic discussion, as waste acids differ widely in composition.

General factors of process economics.

Availability of the olivine is no problem; it is the cheapest neutralizing agent available. Size reduction of the olivine is necessary, power requirements are about 20 KWh/tonne.

With concentrated acid the reaction sustains itself, because it is highly exothermic. A major capital investment is formed by the silica filtration unit, but revenues for the dried silica will be rather high. If acids of a relatively low concentration have to be neutralized, the exothermicity of the reaction will be largely lost. In order to keep the reaction rate at an acceptable level in those situations, olivine should be added in overdose and additional heating may be required. On the other hand, it will not be profitable to separate the silica in those cases, which lowers the capital investments needed.

In some situations it may be interesting to mix olivine and mining-tailings with a high acid potential, in order to achieve an in-situ neutralization. At the moment this is tested in the laboratorium. Equipment for the removal of heavy metals and iron will have to be disigned separately, due to the large differences in waste acid composition. At the moment investigations concerned with the application of the micro-silica are running; prospects so far indicate prices in the range of $300,- / $600,- per tonne.

ACKNOWLEDGEMENTS

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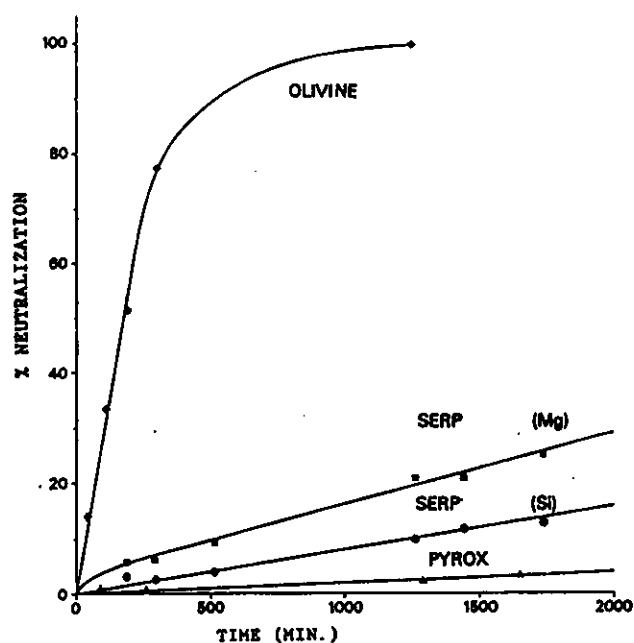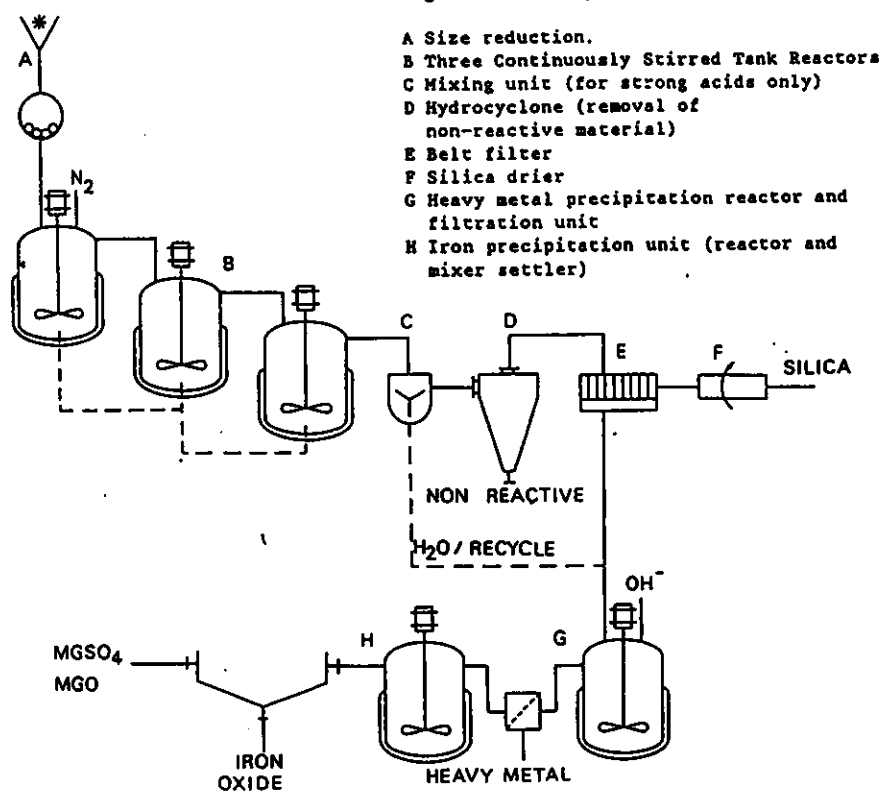[24] Stumm,W. and Morgan,J.J. (1981) Aquatic Chemistry, 2nd ed., John Wiley, New York.

Fig. 1. Reaction rates of a number of magnesiumsilicates. Serpentine
shows incongruent dissolution behaviour as a result of its network
structure of linked silica tetrahedra. Reaction rate of olivine is at
least ten times higher than the other minerals.
Reaction conditions: 500 mg mineral in 500 ml H_2SO_4, pH 1, 70 ° C.
Specific surface area olivine (forsterite) 1550 cm^2/gram, serpentine
(chrysotile) 7760 cm^2/gram and pyroxene (enstatite) 9400 cm^2/gram.
Analysis ICP-AES, surface area BET-N_2.

Fig. 2. Olivine process flowsheet.

A Size reduction.
B Three Continuously Stirred Tank Reactors
C Mixing unit (for strong acids only)
D Hydrocyclone (removal of
  non-reactive material)
E Belt filter
F Silica drier
G Heavy metal precipitation reactor and
  filtration unit
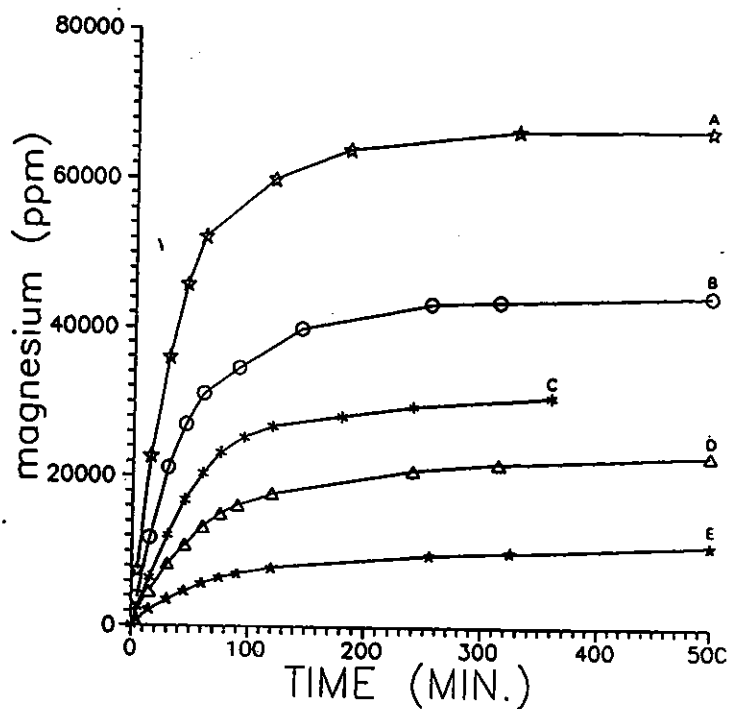H Iron precipitation unit (reactor and
  mixer settler)

Figure 3.

Effect of acid strength on reaction. Batch experiment, olivine grain-size 63 - 250 micron, temp. 85 °C. A) 6N, B) 4N, C) 3N, D) 2N ,E) 1N. The data at T - 500 minutes all represent the calculated theoretical maximum magnesium concentrations wich can be reached (100% neutralization - pH 7).
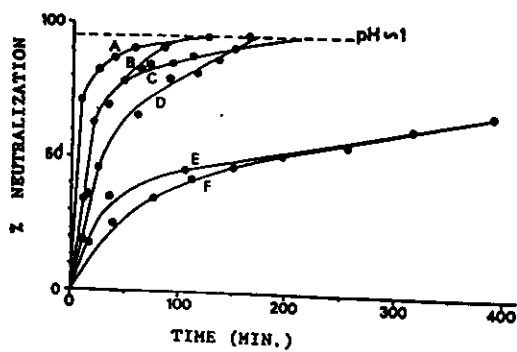

Figure 4.

Effect of temperature on reaction.
Batch experiment, acid strength 3N.
A 90°C H$_2$SO$_4$
B 70°C H$_2$SO$_4$ 15 % extra olivine
C 70°C H$_2$SO$_4$
D 70°C HCl
E 40°C H$_2$SO$_4$
F 40°C HCl
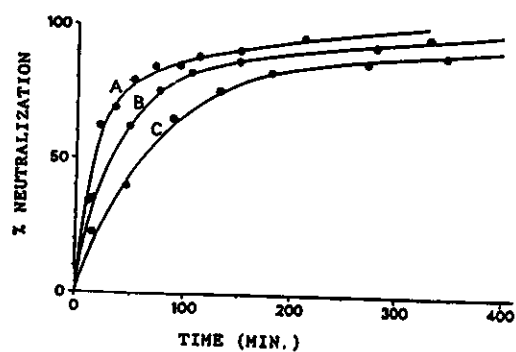
Figure 5.

Effect of grainsize on reaction
A < 63 micron
B < 125 micron
C < 250 micron

Plate 1.

TEM image of silica
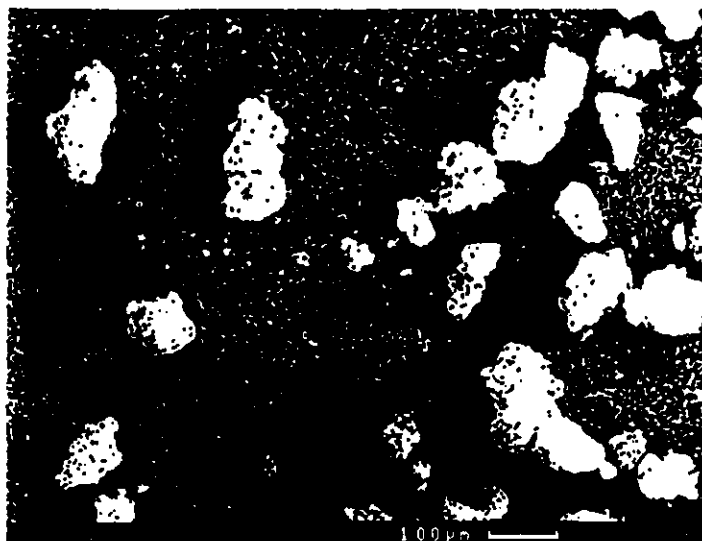(1 cm = 6.26 * 10^{-8} M)
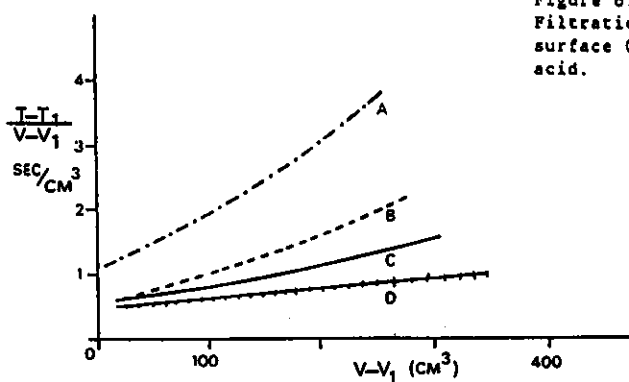

Plate 2.

SEM image of heat-aged silica aggregates.

Figure 6.
Filtration characteristics of silica. Filter press 2 bar, filtration surface 0.01 M^3, filtrate viscosity 7 cPoise, cake thickness 15 mm, 6N acid.   A direct filtration, dilution 30%
            B direct filtration, dilution 100%
            C 22 our heat aging, dilution 30%
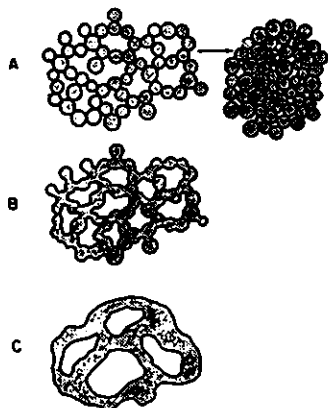   D 22 hour heat aging, dilution 100%

Figure 7.
Stages in aging of a silica-gel. A) gel as formed and dried, shrinks on drying, giving small pore volume and small pore diameter. B) wet heat-aged – increased coalescence. Little shrinkage on drying. C) further heat-aged or autoclaved. Structure coarsened.

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16 may 1988

Mining conference Røros
"The olivine process - waste acid neutralization by reaction
with a magnesium silicate".

Dear Mr. Sveen,

Rereading the paper I send to you last weekend (I suppose you
will get it either today or the 17th), I noticed one small
omission concerning fig. 6.
In the filtration curve presented the formula

$$\frac{t-t_1}{V-V_1} = \frac{r\mu v}{2A^2(-\Delta P)} * (V-V_1) + CL \qquad \text{is used [1] in which}$$

$t-t_1$ = time of constant pressure filtration
$V-V_1$ = corresponding volume of filtrate obtained
r = specific resistance of the cake
μ = viscosity of the filtrate
v = volume of cake deposited by unit volume of filtrate
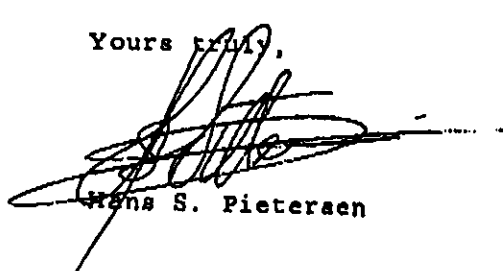A = total crosssectional area of filter cake
ΔP = applied pressure difference
CL = expression for flow a filtrate through filter cloth.

[1] Coulson, J.M. and Richardson,J.F. (1985) Chemical
engineering, volume two, unit operations, p327 , Filtration,
Pergamon Press.

I hope you will be able to put this erratum also in the printed
conference report.

Yours truly,

Hans S. Pietersen

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