INDUSTRIAL POSSIBILITIES OF IDJEN CRATER LAKE WATER

by

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ICHTISAR.

Air Kawah Idjen jang mengandung 600.000 ton belerang (bandingkan dengan tjadangan Indonesia sebanjak sedjuta ton) telah diselidiki mengenai kemungkinan untuk dipakainja sebagai bahan mentah industri.

Meskipun sulfatnja dengan mudah dapat diperoleh dari larutan asam jang entjer itu sebagai gips, telah diusulkan untuk mengolah terus zat achir ini mendjadi ammoniumsulfat (Z.A.), jang merupakan bahan pupuk jang berharga.

Walaupun pengolahan Air Kawah Idjen ternjata mungkin sekali dari sudut teknologi, perlu diselidiki pula kemungkinan meletusnja gunung api tsb., meskipun hal itu telah lama tidak terdjadi.

ABSTRACT.

Idjen Crater Lake Water containing 600.000 tons of sulfur [1] [4] *(compare total Indonesian sulfur reserves of 1 million tons* [2]*) has been investigated as to the possibility of its use as an industrial raw material.*

Although sulfate can most conveniently be recovered from the dilute acid solution as gypsum, it is advantageously suggested to convert the latter into ammonium sulfate, thus potentially increasing the possibility of fertilizer production in Indonesia.

A flowsheet has been proposed.

Although processing the Lake Water seems to be feasible from a technological point of view, a possible danger of Idjen Volcano eruption, however small, should not be overlooked.

I. INTRODUCTION.

Idjen Crater Lake containing 36 million cubic meter of acidic water is situated 20 km birds flight distance North West of Banjuwangi, East Java at an elevation of 2148 m above sea level.

The milky green colored lake water containing free sulfuric and hydrochloric acid has in the past drawn the attention of several investigators.

Van Tongeren [1] submitted a calculation according to which it should be possible to recover from the lake water:

hydrochloric acid
gypsum
alum

Mueller 3) whose commission actually was to look for gypsum sources for the cement industry, suggested the use of Idjen Crater Lake Water as a raw material for gypsum production. In an additional report 4) he suggested to broaden the scope of production and include the manufacture of

- plaster of paris
- carbon dioxide
- aluminum sulfate.

Muellers recommendation was based on the assumption, that although Idjen Volcano is still listed to be active, in view of the volcanoes record of quiescence since the last major eruption in 1817, the risk of an eruption in the near future may not be great. Furthermore it is estimated that a yearly amount of 400.000 cubic meter of lake water can safely be withdrawn from the lake, without an appreciable change of lake water composition, since this is continuously replenished.

In the following only technological aspects will be considered and investigations made into the possibility of suggesting the acidic lake water as an industrial raw material.

II. ANALYSES AND POSSIBILITIES.

Extensive sampling of the lake water has first been carried out by Mueller who collected samples from 32 systematically selected points ranging from 7 to 127 meters below the lake surface (1957).
Average analyses showed the following components:

SO_4''	57.0 g/l
Cl'	17.7 g/l
Al^{+++}	5,08 g/l
$Fe^{++(+++)}$	1,58 g/l
Ca^{++}	0,94 g/l
Mg^{++}	0,63 g/l
Na^{+}	1,05 g/l
K^{+}	0,98 g/l
pH	0,77

Although it is recognized that the composition may vary from point to point and from one season to another, which variation should be taken into consideration in an eventual plant design, it can however be assumed that no principal deviation will occur, so that it was decided to carry out the experiments with a synthetic mixture based on Muellers analysis.

From this free acid containing lake water *sulfate*, *chloride* and *alum* will be taken in consideration for recovery.

1. Chloride.

From the acidic character of the lake water it can be expected that hydrochloric acid can be easily removed from the heated solution, since sulfuric acid has a drecreasing effect on the solubility of HCL gas in water [5].

A maximum gain of HCl can therefore be expected when lake water is directly fractionnated.

The following is a typical distillation showing HCl yields in the various fractions.

Table 1

Fractionnation of 500 ml Idjen Crater Lake Water.

Temp. °C	% distillate	mg HCl in distillate	% HCl (cumulative) in distillate
96.6 — 96.9	0 — 40	1.25	—
96.9 — 97.0	40 — 60	1.25	—
97.0 — 98.0	60 — 70	3.36	—
98.0 — 100.0	70 — 75	6.95	0.14
100 — 107	75 — 80	17.88	0.34
107 — 108.5	80 — 85	2140	23.9
108.5 — 110	85 — 90	4220	70.2
> 110	90 — 95	1870	90.6

For recovering 90.6% of the hydrochloric acid, 95% of the solution has to be distilled in which most of the gas is collected in the final 15% of distillate.

The HCl — H_2O vapor liquid equilibrium diagram is known to have a maximum boiling point corresponding with an azeotropic mixture consisting of 20% HCl.

Recovery of HCl not only requires distillation of the major part of the Lake Water in acid resistant equipment, but also a maximum strength of 20% HCl only can be expected which compares unfavorably with the 35% of commercial solutions.

It is doubtful whether dilute hydrochloric acid recovered in this way can compete with concentrated acid from the electrolysis process, which for some time to come will remain a relatively „cheap" byproduct in Indonesia, for which the demand is still limited [6].

Leaving hydrochloric acid in the solution moreover facilitates the recovery of sulfate as pure gypsum (see II.3).

2. Alum.

Aluminum contents can theoretically be recovered from the lake water as alum (potassium aluminum sulfate) or aluminum sulfate.

Compared with commercial processes for the production of aluminum sulfate, in which bauxite (53% Al_2O_3) and 50° Bé sulfuric acid are reacted or the manufacturing of alum, which starts from aluminum sulfate, it should be obvious that compared to it, lake water is a dilute and impure (Fe and Cl containing) raw material, which first of all needs concentration in expensive acid resistant equipment, finally however yielding a product, which is impure.

Although it has been shown by Eimco [7]) that aluminumsulfate production from lake water is chemically feasible, it remains to be seen whether alum production can economically be based on Idjen Crater Lake Water as a raw material.

3. Sulfate.

Idjen Crater Lake Water can probably best be regarded as a dilute sulfur source, which should be concentrated before applying it as an industrial raw material.

This concentration step can easily be carried out by adding crushed limestone to the acidic lake water at atmospheric temperature thus easily yielding gypsum precipitate (table 2), which can be seperated from the bulk of the lake water and can be regarded as a more concentrated raw material.

While for this concentration step no fuel is required, this operation at less acidity is another advantage from the point of view of materials of construction.

Basically the following reaction takes place:

$$H_2SO_4 \text{ (lake water)} + CaCO_3 + H_2O \longrightarrow CaSO_4.\ 2\ aq + CO_2$$

The gas evolved provides a stirring action, which is beneficial to the proceeding of the reaction.

At pH higher than 3.0 side reactions will occur, causing impurities to be incorporated in the gypsum precipitate

$$Al^{3+} + 3H_2O \longrightarrow Al(OH)_3 + 3H^+$$
$$Fe^{3+} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^+$$

so that an increased yield will necessarily imply a purity decrease of the fina product.

Conditions of gypsum recovery have been described by Eimco [7]) .

III. FURTHER UTILIZATION OF GYPSUM.

Although from the above, conversion of Idjen Crater Lake Water into gypsum seems to be the only feasible possibility, production of this inexpensive commodity for direct consumption in the cement industry as suggested by Mueller 5) is not too attractive, if we bear in mind that a relatively substantial investment will be required for this project. (a.o. a 25.000 meter acid resistant pipe line from the crater lake to the plantsite).

Furthermore it is indicated by Mueller) that due to the apparent absence of limestone deposits of good quality in the neighbourhood of Banjuwangi, this should be procured from elsewhere (it is even suggested from Gresik area, to make use of the crushing facilities of the cement plant) so that two way transportation of bulky material (limestone and gypsum) will be needed.

In view of the above, it is suggested here to process the gypsum further into ammoniumsulfate according to the Merseburg process. Reasons for this proposal will be obvious from the following reactions:

$$\begin{array}{lll} H_2SO_4\ (\text{lake water}) + CaCO_3 + H_2O & \longrightarrow CaSO_4.2\ aq + CO_2 & *) \\ 2\ NH_3 + CO_2 + H_2O & \longrightarrow (NH_3)_2\,CO_3 & **) \\ CaSO_4.2\ aq + (NH_4)_2CO_3 & \longrightarrow CaCO_3 + (NH_4)_2SO_4 + 2H_2O & ***) \\ \hline & & + \\ H_2SO_4\ (\text{lake water}) + 2NH_3 & \longrightarrow (NH_4)_2SO_4 & \end{array}$$

a). The final product, ammoniumsulfate is a fertilizer, valuable in increasing food production in Indonesia.

b). Since $CaCO_3$ is recycled, theoretically no limestone will be required for above process.

c). CO_2 evolved in the gypsum production (*), can be completely utilized in the conversion into fertilizer. ***)

d) $CaCO_3$ and gypsum are already in a fine state as precipitates, so that the grinding operation normaly required, can be omitted here. Furthermore increased reaction rates may be expected.

e). Above plant can eventually be regarded as an extension of the intended Gresik fertilizer plant in which however the sulfate required can be obtained from local sources (lake water). As such it can be suggested to ship the required ammonia as liquid in tankcars from Gresik to the the plant site.

f). Theoretical output.
If 400.000 m^3 of lake water per year containing 57g SO_4/liter will be processed at 90% yield, the ammoniumsulfate production will be:

$$\frac{132}{96} \times 0.90 \times 400.000 \times 57\ \text{kg} = 28.000\ \text{tons per year.}$$

In developing a process for the manufacture of ammoniumsulfate from Lake Water the attached flowsheet is suggested.

IV. INTENDED PROCESS.

Idjen Crater Lake Water is reacted with a slurry of recycled precipitated $CaCO_3$ (plus make up) in a *Gypsum Reactor* at room temperature.

$$H_2SO_4 + CaCO_3 + H_2O \longrightarrow CaSO_4.2\,aq + CO_2$$

CO_2 gas evolved is stored and will be used with NH_3 for making ammonium arbonate solution for the Merseburg reaction.

The underflow from the Gypsum Reactor is filtered, and the waste liquor discarded. The filtered gypsum, which has a purity of at least 85% is forwarded to the *Merseburg Reactor,* in which double decomposition takes place as follows:

$$CaSO_4.2aq + (NH_4)^2CO_3 \longrightarrow CaCO_3 + (NH_4)^2\,SO_4$$

The filtered and washed $CaCO_3$ is cycled back to the gypsum reactor, while the ammonium sulfate solution freed from NH_3 and CO_2 by heating is concentrated and crystallised, finally yielding dry ammoniumsulfate crystals for fertilizing purposes.

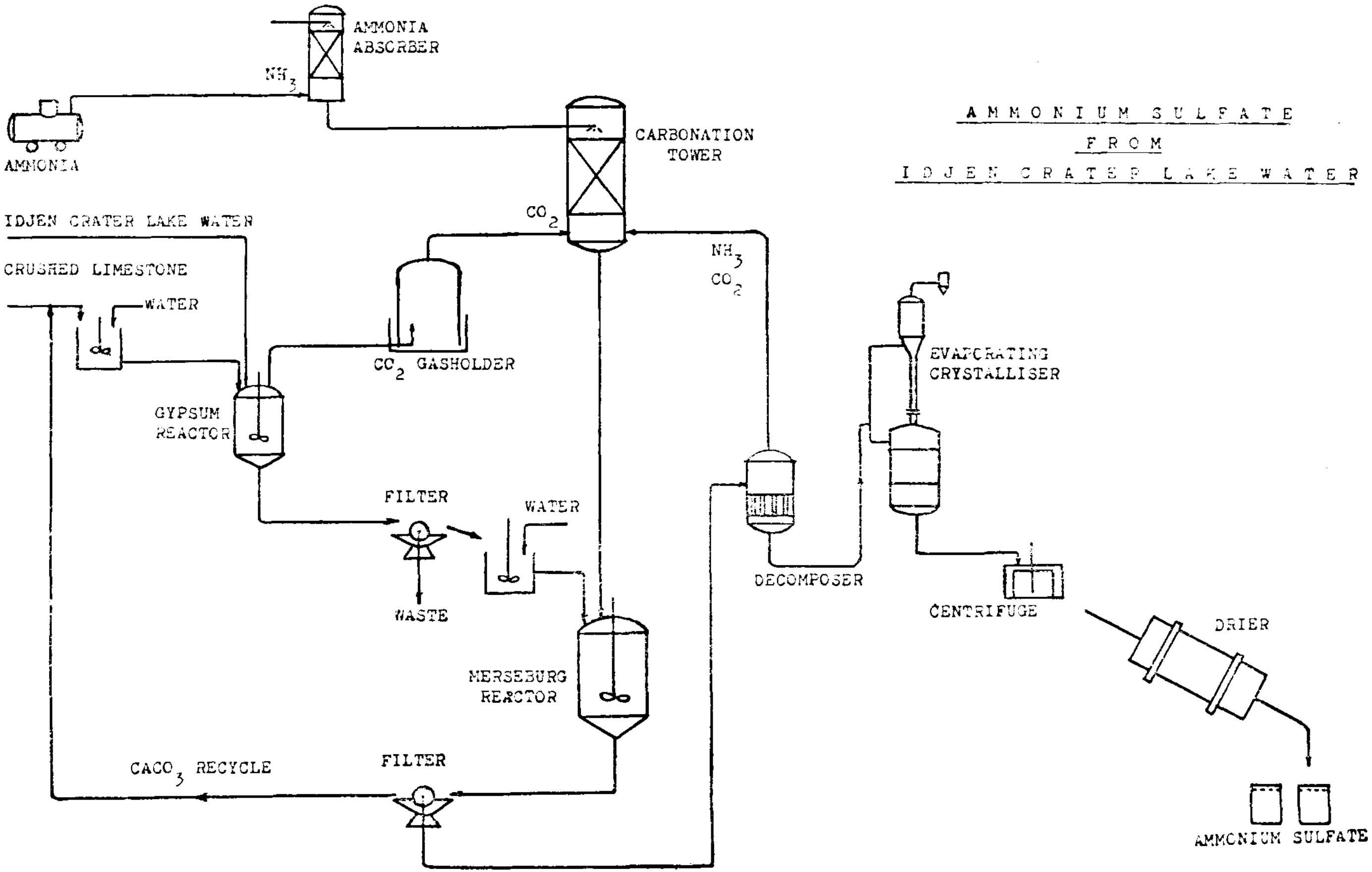
In the flow diagram proposed the following will be checked:

1. Gypsum preparation:
   Yield, purity of gypsum obtained and amount of limestone required.
2. Washing of gypsum cake with Lake Water.
3. Ammoniumsulfate preparation. (Mersebuig reaction).
   a) reaction conditions.
   b) influence of impurities on yield.
4. Yield and purity of gypsum from impure $CaCO_3$
   (possibility of recycling impure $CaCO_3$ from the Merseburg reactor).

V. EXPERIMENTAL PART.

1. Gypsum preparation.

Lake water is stirred with varying molar proportions of 20% $CaCO_3$ slurry at room temperature, resulting in 71,5 — 93,0% yields with 95,0 — 78,0% purity (table 2).



AMMONIUM SULFATE FROM IDJEN CRATER LAKE WATER

Table 2

Purity and Yield of Gypsum produced from and washed with Lake Water.

	Raw Material			Product $CaSO_4$, 2 aq				Waste Liquor	Wash Liq	Washed Product			SO_4 consumption per gr. SO_4 recovered			Waste Wash Liq.
Test No.	ml Lake Water a	gr. CaCo$_3$ b	% mole ratio Ca/SO_4 c	gr. Yield d	% Purity e	% Yield (SO_4 basis) f	% Yield (CaO basis) g	pH h	ml. Lake Water j	% Purity k	gr. Yield l	% Yield l/d m	Reaction a/l o	Washing j/l p	Total o + p q	pH r
1.	250	11.89	80	19.21	95.0	71.5	89.5	3.0	22.1	96.6	17.12	94.0	1.54	0.136	1.676	2.8
2.	250	13.37	90	21.20	94.5	78.5	87.0	3.5	24.8	95.7	19.0	94.9	1.38	0.136	1.516	2.8
3.	250	14.85	100	26.27	87.1	89.8	89.6	4.2	81.2	98.6	20.82	90.8	1.24	0.403	1.643	2.8
4.	250	16.35	110	28.42	81.7	90.0	82.5	4.2	105.0	94.4	22.42	97.9	1.205	0.505	1.710	2.8
5.	250	17.84	120	30.41	78.0	93.0	77.4	5.0	149.0	89.4	23.65	99.6	1.205	0.716	1.921	2.7

Note:

1. Prec. $CaCO_3$ (99,6 %) applied as 20 % slurry — b)
2. Reaction time 30 min., mixture stirred at 150 rpm.
3. Precipitate washed with 500 ml. distilled water and dried at 60°C — d).
4. % Purity indicates $CaSO_4$, 2aq. content in product — e).
   (Al and Fe hydroxides independently determined).
5. Amount of SO_4 + Cl in wash liquid — j) equivalent with Al and Fe hydroxides in gypsum cakes.

Whether a high purity at low yield or low purity at high yield of product will be preferred should be checked with results of the Merseburg reaction.

It should however be noted that

i) not all sulfate from the lake water will be recovered.

ii) part of the $CaCO_3$ used will dissolve and will be wasted in the waste liquor as $CaCl_2$.

iii) the product will contain impurities of $Al(OH)_3$ and $Fe(OH)_3$ which will be precipitated under the conditions of the reaction.

2. Washing of gypsum cake.

In the above it is stated that the gypsum precipitated in the reaction between lake water and $CaCO_3$ will contain Al and Fe hydroxides as impurities. It is expected that these impurities will not dissolve in the ammoniumsulfate reaction and so will be returned to the gypsum reactor together with the precipated $CaCO_3$. Any eventual build up as a result of this impurities recycle should however be avoided.

Washing of one of the cakes with lake water as the logical acid available, indicaties a washing time of 90 minutes to be sufficient to dissolve the greater part of the impurites (see table 3).

Table 3

Impurities dissolved in washing gypsum (purity 82%) with 100% equivalent of Lake Water.

Minutes	% Impurities in gypsum (dry basis)	% impurities dissolved from cake
0	18.0	0
10	17.4	3.4
30	9.8	45.6
60	8.9	50.6
90	5.9	67.2
100	5.86	67.2

Note: Gypsum cake as a 10% slurry is stired (300 rpm) with 100% equivalent of lake water, filtered and washed.

Based on the above, washing experiments of the impure gypsum from the gypsum reactor with acidic lake water, to remove any undesirable high content of hydroxides, (from the various gypsum cakes obtained in V.1).

have been carried out with a washing time of 90 minutes and 100% equivalent of lake water and the results (acid consumption versus purity obtained) tabled in table 2.

Total requirement of lake water needed for gypsum precipitation and washing has also been included in this table.

Results fromt able 2 indicate that purities of the gypsum precipitation from lake water can sufficiently be increased to 89% and higher by washing with an equivalent amount of lake water at a favourable yield (91% and better).

3. Merseburg reaction.

Ammoniumsulfate is prepared industrially from gypsum or anhydrite with NH_3 and CO_2 gas according to the double decomposition reaction as follows.
$CaSO_4 + (NH_4)_2CO_3 \longrightarrow (NH_4)_2SO_4 + CaCO_3$ (Merseburg reaction) [8]
In the particular condition the gypsum required is already inafine state, which. needs a shorter reaction time if compared to similar applications elsewhere [9]

a) **Reaction time and temperature**

Reaction time required has been followed at room and somewhat elevated temperature in reacting 20% gypsum slurry at atmospheric pressure with an equivalent amount of $(NH_4)_2CO_3$ solution, containing excess NH_3 (NH_3/CO_2 molar ratio: 2,07), resulting in a liquor containing 12,5% $(NH_4)_2SO_4$.

Table 4

% Conversion of gypsum in the Merseburg reaction

	% conversion = $\frac{CaSO_4 \text{ reacted}}{CaSO_3 \text{ initial}}$	
Time	Temp.: 26°C. pure gypsum used	Temp. 37 — 38°C. gypsum of 87.05% purity
5	68	—
7	—	84.5
10	80	—
15	82.5	90.8
20	88.5	91.9
30	94.8	95.3
35	—	95.2
60	95.2	—
120	95.2	—

With 35 minutes reaction time at room temperature, a 95% yield is obtained which is comparable to results obtained in industry [10]

b) **Yield of $(NH_4)_2SO_4$ from gypsum of variable purity.**

Reacting Lake Water wih different quantities of $CaCO_3$ will result in a gypsum precipitate of different purities (see table 2).
As these may have its effect on the Merseburg reaction, different gypsum precipitates have been reacted with $(NH_4)_2CO_3$ as under a) during 35 minutes at room temperature.

Table 5

% conversion in Merseburg reaction, reacting gypsum of variable purity.

Purity gypsum %	% conversion
100	95.2
92.2	95.1
88	95.0
87.1	95.2
85	95.1
84.7	92.0
78	92.1

Gypsum of 85% purity and better easily results in a 95% conversion into ammoniumsulfate, when the reaction is carried out at room temperature during 35 minutes.

4. Gypsum prepared from impure $CaCO_3$.

Whereas the experiments in table 2 were carried out with pure $CaCO_3$, the question is raised whether Al and Fe hydroxides containing impure $CaCO_3$ can be used in the gypsum conversion in order to know the recycling possibilities of $CaCO_3$ from the Merseburg reaction.

Table 6

Gypsum from impure $CaCO_3$ samples.

Analysis of $CaCO_3$			Yield Cake gram	Gypsum purity %	$\frac{SO_4 \text{ in prod.}}{SO_4 \text{ available}}$	pH waste liquor
% $CaCO_3$	% $CaSO_4 \cdot 2aq$	Impurities $Al(OH)_3 +$ $Fe(OH)_3$				
100	—	—	10.54	87.1	89.8	4.2
91.4	6.7	1.9	11.0	87.0	90.0	4.2
87	6.36	6.64	10.92	86.8	89.0	4.2
78.8	5.78	15.42	11.01	86.6	89.3	4.2
74.6	6.05	19.35	11.0	86.4	89.4	4.2
67.2	8.79	24.01	13.1	73.8	88.2	4.4

Note: Each sample containing 5.94 g pure $CaCO_3$ is reacted with equivalent amount (100 ml) of lake water during 30 minutes.

Conclusion: If lime stone finally applied to the gypsum reactor (recycle + make up) has a purity of at least 74.6%, gypsum of a fairly constant purity (86 — 87%) will be produced.

Since only purities of 85% are required for a good conversion in the Merseburg reaction (V.3), above results give an indication that washing of the gypsum as discussed under V.2 is superfluous.

Based on a gypsum feed to the Merseburg reactor of 86% purity, it can be calculated that lime stone make up for compensating losses in the waste liquor from the gypsum reactor amounts to 11.8% with a minimum required purity of 95 % thus making the ammoniumsulfate manufacturing from Idjen Crater Lake Water according to Merseburg with $CaCO_3$ to be recycled, a feasible process.

ACKNOWLEDGEMENT.

Financial aid from the Ministry of Higher Education for this investigation is herewith kindly acknowledged. Thanks are due to Miss Siti Aminah Soepojo, Messrs Adrima Amadar and Njoman Sudibia for their contribution to the experiments in this work.

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