

Botany. — *On the cause of the high acidity in natural waters, especially in brines.* By L. G. M. BAAS BECKING. (From the Botanical Institute, Government University, Leyden, Holland.)

(Communicated at the meeting of November 26, 1938.)

I. On several excursions to salt lakes, solar salt works and volcanic lakes the author noticed high actual acidities. On a trip to Australia and to the Dutch East Indies in 1936 he noticed three remarkable instances of high acidity which, apparently, showed no relation but which proved, after analysis, to possess a common cause.

a. Lake Tyrrell, a salt lake in North-West Victoria, visited April 1936 with Dr. J. REUTER, Mr. CHAS. A. BARRETT and Mr. A. D. HARDY. Shallow, salt-saturated pools of this lake showed an acidity of around $\text{pH} = 3.00$ which was checked in the laboratory electrometrically as $\text{pH} = 2.98$.

b. Kawah Tjiwedéh, a hot volcanic lake in Central Java, visited May 1936 with Mr. H. JAPING of the Forestry Service and Dr. J. REUTER. A $\text{pH} = 2.10$ could be determined electrometrically.

c. The solar evaporation of seawater on the Island of Madura at Gersik Putih visited June 1936 with Dr. J. REUTER. In the denser brines of the shallow evaporation-pans a $\text{pH} < 5.0$ could be observed.

II. High acidities have been repeatedly recorded in the literature, a survey of which may be found in an article of WALDEMAR OHLE (20). It appears that, in certain instances, even a negative pH occurs in natural waters. (Oral communication by G. W. HARMSSEN.)

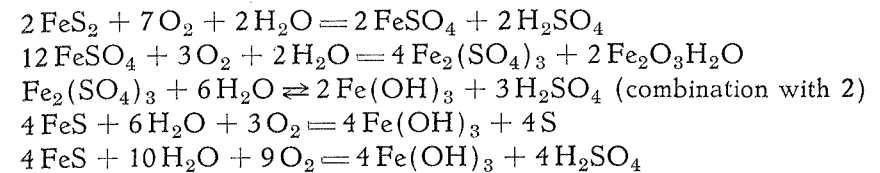
As to the cause of these acidities the authors do not agree — it may be useful to enumerate the factors that contribute to the acidity of natural waters.

The acidity is due to geochemical factors:

1. The acid is contributed directly by the mineral environment. Examples: volcanic lakes (HCl , H_2SO_4 : RUTTEN (25), JUNGHUHN (17), WOLTERECK (39), CLARKE (9)).

2. The acid is formed by hydrolysis of salts of heavy metal. Alum lakes in Western Australia (SIMPSON, 27). Hydrolysis of FeSO_4 or $\text{Fe}_2(\text{SO}_4)_3$ (OHLE (20), SKADOVSKY (28)).

3. The acid is formed by oxidation (weathering) of sulphides, such as pyrite (FeS_2 regular), marcassite (FeS_2 rhombic), troilite (FeS) or hydro-troilite (FeS , $n \text{H}_2\text{O}$, colloidal) according to:



(VIRCHOW 34, SCHÄPERCLAUS 26, HÖGBOM 13, JEWELL 16, UÉNO 33).

The acidity is due to biological factors.

4. The acidity is due to carbon dioxide. This has been claimed by HÖLL (14) for the high acidity of peat-bog-water. The conclusions of this author were probably based on data obtained by means of an unsuitable titration-method (BAAS BECKING and NICOLAI (4)).

5. Humic acids contribute to the acidity of bog waters (ODÉN (19), WEHRLE (36)).

6. The cell walls of plants excrete acids (claimed for bog water by PAUL (21)). This hypothesis has in recent years lost much of its attractiveness.

7. The acids liberated in the bacterial decomposition of (e.g.) cellulose.

8. Base-exchange on cell walls or protoplasm is the cause of the high acidity of bog water which is poor in electrolyte and may contribute to the high acidity of the cell sap of plant cells submerged in any type of aqueous milieu (BAUMANN und GULLY (5), SKENE (29), STELMACH (30), BAAS BECKING and NICOLAI (4), WIRTH and RIGG (38), THOMPSON, LORAH and RIGG (31), WILLIAMS and THOMPSON (37)). This factor seems well established and may account quantitatively for the acidity of many waters.

9. Bacterial oxidation of sulphides, whether pyrite, marcassite or troilite. This process would be indistinguishable, on first sight, from the geochemical oxidation (HARMSSEN 11, WAKSMAN 35).

III. Further description of the waters examined.

1. *Lake Tyrrell.* After Lake Corangamite, the largest lake in Victoria. It occupies an area of ± 66 sq. miles and is situated $\pm 142^\circ 50' \text{E } 35^\circ 10' \text{S}$. During the rainy season it is fed from the South by Tyrrell creek which is an offshoot of the Avoca river, the source of which is on the N-slopes of the Dividing Ranges.

The Victoria State Water Supply Commission, through the kindness of Mr. A. D. HARDY put at the disposal of the author a number of borings made in the neighbourhood of the lake which show 50—100 ft of clay which rests either on red sandstone or on a black carboniferous clay, often containing lignite. This clay continues to a depth of sometimes 600—800 ft. At the time of our visit (11—IV—'36) salt had been harvested on the lake — the scraped floor glistened with brine and curious, scroll-shaped efflorescences of NaCl , about an inch high. The crust rested on top of a sand without FeS , but strongly smelling of H_2S ; bright yellow patches

occurred in the soil which became orange on exposure to the air. With the universal indicator a pH of < 3 could be determined while the index of refraction pointed to a $\pm 22\%$ solution. On microscopic examination the following living organisms were met; 1. The cosmopolitan salt-diatom *Amphora coffaeiformis* Ag, 2. The cosmopolitan salt flagellate *Dunaliella spec.*; 3. Bacterial zoogloea; 4. A unclassifiable ciliate. At a greater depth (± 1 foot) true black mud ($\text{FeS} \cdot n\text{H}_2\text{O}$) occurred. From the brine-soaked soil samples we could isolate fly larvae and nematodes. From the brine samples which we collected in sterile vessels we isolated at Leyden aerobic sulphur bacteria, sulphate reducers and anaerobic cellulose fermenting bacteria. Analyses of this brine were carried out at the Laboratory of Inorganic Chemistry at Leyden and by Mr. H. BOOY at the Botanical Laboratory. The results are given in Table I.

TABLE I.

	Percent		Normality		Totaal normality (average)
	Sample 1	Sample 2	Sample 1	Sample 2	
Na ⁺	7.93	7.88	3.45	3.43	kations 4.245
K ⁺	0.10		0.03		
Mg ⁺⁺	0.93	0.94	0.77	0.78	
Fe ⁺⁺	0.004		0.002		
SO ₄ ⁼	2.14	2.27	0.43	0.47	
Cl ⁻	13.76	13.65	3.88	3.85	anions 4.315

The difference between the cation and anion equivalents equals 0.070 aeq. of which only 0.001 is H⁺ (pH = 2.98). Mr. BOOY found in this brine not more than 0.002 aeq. Ca⁺⁺, but as considerable difficulty was experienced by him in the calcium determination in these concentrated brines it may very well be that the amount is much too low. The colorimetric iron determination checked very well with both a colorimetric and an electro-metric titration curve of Mr. BOOY, in which the "bufferplateau" between pH = 4 and pH = 5 required about 2 milli-equivalents of base.

Aluminium could not be detected. The cause of the high acidity remained obscure until we obtained further experience from the Madura-brines (see below).

2. The volcanic lake Kawah Tjiwedéh proved to contain enough sulphuric acid to cause the low pH. As the acid waters issue from the soil at temperatures of over 90°C. this is apparently an example of non-bacterial origin of this acid.

A. Description.

3. *Salterns at Gersik Putih, Madura.* With the collaboration of Dr. J. REUTER and several gentlemen from the "Government Salt Regie" *) we were also able to gather a large number of data in a week's work.

The Government Salt Lands at Gersik Putih consist of ninety units (= salt pans) each about 3.5 Hectare (± 9.6 acres) in area. Two large sloughs ("voorboezem" and "binnenboezem") furnish the contact with the ocean waters. One sixth of the area of one pan is destined for the crystallizer-tables, the other five-sixths are divided into a series of reservoirs. The concentration process is only feasible in the dry East Monsoon, during the West Monsoon the pans are flooded with sea water. At the end of the West Monsoon this water is drained off and tables and reservoirs are cleaned and rolled. From the second slough water is let in and as soon as the water on the table reaches a concentration of 4—5° Bé the water is drained to the fifth reservoir and the table floor is dried and rolled again. This drying often causes cracks in the bottom which do not occur when stronger brine is applied. The table is drained again when the concentration mounts to 16—18° Bé. As soon as the concentration increases to 25° Bé, initiating the precipitation of the first NaCl, the table is drained and rolled for the last time before the inlet of the concentrated brine out of which salt is made. The conditions for this "inlet" are reached about on the 25th day of the campaign. A stationary state is then maintained for several weeks in which the following depths of the brine and concentrations are maintained on the pans.

TABLE II.

Reservoir	Comparative Area (v = unity)	Depth of liquid in cm	Concentr. in ° Bé
I	7.5	4—30	4.5—6
II	4.7	4—6	9
III	2.6	4	14
IV	1.6	4	16
V	1.0	4	23
Table	3.5	4	23—dry

At the native salt lands of Sūmenep the interval between the beginning of the campaign and the inlet is much greater, about 45 days. At these lands

*) The author's thanks are due to Mr. P. H. JORDAAN C.E., Mr. F. E. VAN HAEFTEN, Chem.E., Mr. N. G. W. WINIA and Mr. H. S. STELTER not only for energetic and efficient assistance but also for many valuable suggestions.

the reservoirs are not cleaned as scrupulously as at the Government Lands, so that the conditions for the development of various organisms are better at Sūmenep.

B. Organisms.

At Gersik Putih, however, a mass of organisms occurred both in the reservoirs and on the tables, apparently developing in a very short time.

The most conspicuous of these organisms are:

1. *Ruppia maritima* L. var. *a rostellata* KOCH occurring in brines up to 6° Bé. This cosmopolitan form was also found by the author in South Australian salt lakes and marine salterns; moreover in marine salterns at Dadar, near Bombay and at Setubal, Portugal. Its upper limit of growth seems to be situated at $\pm 9^\circ$ Bé (see WOOD and BAAS BECKING (40)).

2. *Microcoleus chthonoplastes* Thur. This cosmopolitan bluegreen alga forms linoleum-like mats in salt lakes all over the world. To the mediterranean "briners" this mass is known as "feutre dol" and is used in some instances, as a groundcover of the salt pans to ensure a clean harvest. CAVARA (8) and also Miss HOF (12) have shown that the alga is halotolerant.

3. *Enteromorpha*, *Chaetomorpha* and *Cladophora* were numerous in the first reservoirs. These reservoirs may be used as fish ponds to advantage, for the fish live on the bluegreen algal mat (called by the Fisheries Inspector "short" algae, in contradistinction to the "long" algae, which float and are the chlorophyceous forms mentioned above). The "long" algae are removed for they are a veritable incubator for mosquito-larvae, which larvae hide in the algal mass and so cannot be reached by a very efficient Javanese mosquito fish, *Haplochilus panchax*, which is also halotolerant.

4. The other, more typical "salt" organisms of the Gersik Putih salt lands will be described at another place, suffice it to say that many of them could only be found in pits on the abandoned salt land "Nembakor-West", where the brine had remained undisturbed for over a year showing that, owing to the "haste" of the salt campaign, their usual incubation time could not be exceeded normally. (The same phenomenon was observed near Bombay, where the typical halophilic flora and fauna only occurred in discard pits and byways containing stagnant water).

The *Ruppia*, mentioned above, is almost quantitatively taken out of the reservoirs. The removal of green- and bluegreen algae is never so successful.

5. Up to the highest concentration we either observed or deduced the presence of several groups of bacteria, which observations and deductions were further verified in the laboratory.

- a. purple sulphur bacteria
- b. sulphate reducing bacteria
- c. aerobic sulphur bacteria

- d. iron bacteria
- e. anaerobic cellulose-bacteria.

a. The purple sulphur bacteria occurred in brines, independent of concentration, in which the pH was higher than 8.2, in agreement with the beautiful work of VAN NIEL (18).

b. The sulphate reducers seemed omnipresent, a tough, elastic black mud occurring everywhere a few millimeters under the surface of the reservoirs and tables. Only after previous drying and cleaning the black layer was covered with colloidal $\text{Fe}(\text{OH})_3$.

c. The aerobic sulphur bacteria occurred in a thin, grayish skin at the surface of the reservoirs and tables, especially after aeration and cleaning.

d. The iron bacteria showed after aeration in the colloidal $\text{Fe}(\text{OH})_3$. Especially the genus *Gallionella* was found repeatedly even in solutions as high as 19° Bé at temperatures of 34° C. (contrary to the expectations of CHOLODNY (9), BUTKEWITCH (7) and PERFILIEV (23) see also HARMSSEN (11)).

e. Anaerobic cellulose fermentation was demonstrated in the laboratory to be exceedingly active.

In a few months large quantities of filter paper were almost completely dissolved.

The author shall have occasion to treat the above mentioned groups of bacteria and their mutual relation later in this paper.

C. Field determination.

The following meteorological and chemical data were gathered;

1. Intensity of visible radiation during the day.
2. Absorption of visible radiation by various brines.

These determinations were carried out by means of an especially designed instrument, which will be described in another publication.

3. Evaporation on a black and on a white surface, by means of simple evaporating trays, which will be also described elsewhere.

4. Air- and brine-temperatures as a function of density of the brine and time of the day.

5. Hydrogen-ion concentration, colorimetrically, by means of a "La Motte" comparator. We also made use occasionally of the "Universal-Indikator" to determine the range.

6. Specific gravity was determined by means of areometers of different make.

7. Refractive index was determined by means of a "Tomatenrefraktometer" of Zeiss. This handy little instrument only requires a drop of solution for a determination and gives, after recalibration and correction for temperature, quite accurate results.

8. Chemical determinations were carried out in an improvised "laboratory" constructed near the salt pans and also at the chemical laboratory

of the Salt Regie at Sūmenep. These determinations comprised chloride, sulphate, total titratable base and hydrogen sulphide.

As the increase in concentration in the subsequent reservoirs and tables gave us, in one morning, an almost continuous series of observations, a solar salt work presents almost ideal conditions for hydrobiological work.

Instead of recording all the data collected the author shall confine himself to a graphical illustration of a few particular instances.

Figure 1 gives the Temperature, pH, Excess Base (in aequivalents) and Per cent Transmission for visible radiation of 5 cm brine of June 7th, 1936,

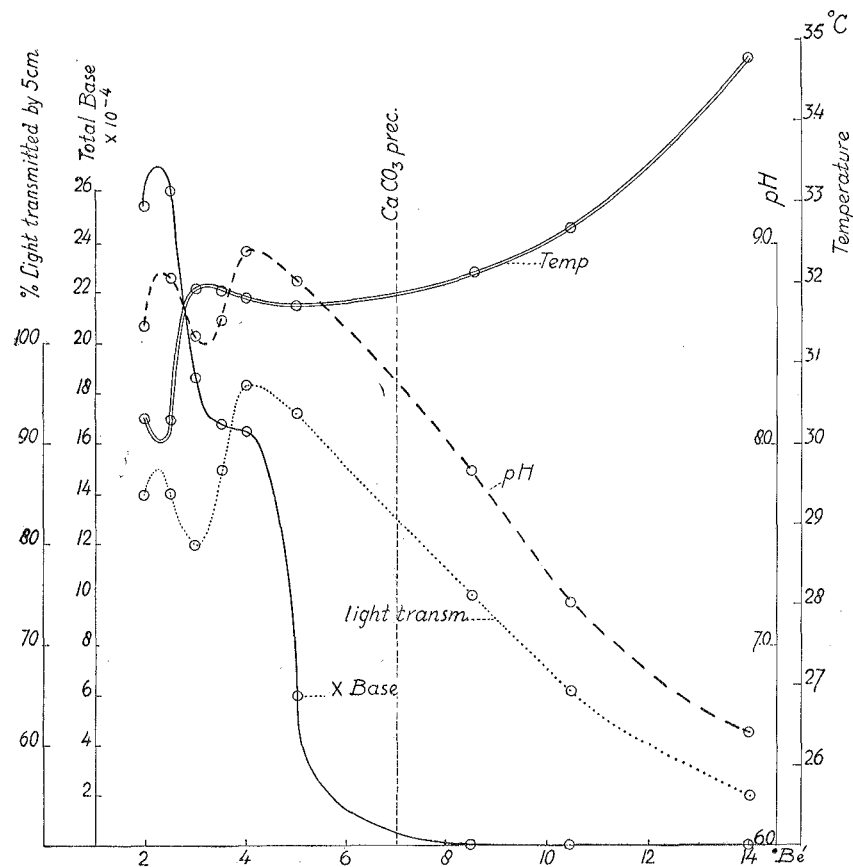


Fig. 1.

11—12 a.m. The abscissa gives the density of the 5 reservoirs and 3 pans in degrees Baumé.

1. Excess base, which is a good index for the amount of CaCO_3 in solution. Determined by titration with approx. 0.01N HCl with methyl red indicator.

The lime has almost quantitatively disappeared from the water at 8° Bé. USIGLIO (32) found in experimental evaporation of seawater the CaCO_3 precipitating at s.g. 1.050, corresponding to 7° Bé. Apparently, in our case,

the precipitation occurs at lower densities. We found, however, that, in other instances the deposition of lime was much retarded. Roughly speaking it depends upon the amount of algae present in the water, as in the recently cleaned reservoirs the lime was often "overdue".

The algae, by using the bicarbonate in their photosynthesis, according to $2\text{HCO}_3^- \rightarrow \text{H}_2\text{CO}_3 + \text{CO}_3^{2-}$ will increase the carbonate concentration so that the solubility product of the carbonate may be reached. This goes parallel with an increase in alkalinity (see pH, fig. 1). Whether, like AHRENS (1, 2) claims for higher plants, the algae are also able to excrete $\text{Ca}(\text{OH})_2$ seems probable after the work of HUBERT.

2. Light transmission and

3. pH show much the same picture. On the places of steepest decline in the excess base, both pH and light transmission decrease rapidly while on the places where the excess-base changes but slowly, both light transmission and pH increase. It may be that the small particles of CaCO_3 cause a slight cloudiness in the water prior to sedimentation.

4. In the more turbid solutions the temperature increases rapidly. Superimposed upon this effect is the increase of temperature with concentration, caused by the decreasing evaporation-capacity and by the decrease in specific heat. The picture given in figure 1 is specific for the pan studied as all salt pans show individual differences. This first stage in salt-making, called the "condensor" or "pickle-pond" stage depends therefore upon the photosynthetic activity of green organisms. In certain reservoirs the pH increases to 9.4.

We may say that, at a concentration of approximately 10° Bé the water is free from lime, and practically free from buffer. Small amounts of acids and bases may now change its actual acidity. It now concentrates until, at 16—18° Bé, gypsum will precipitate (USIGLIO 32).

$\text{CaSO}_4 \cdot 2 \text{ aq}$ easily forms colloidal solutions which are, in salt works in temperate regions, clarified by the action of a phyllopod crustacean *Artemia salina* L. (RACKETT 24, PAYEN et AUDOUIN 22, BAAS BECKING 3). This "brine-shrimp", however, does not occur at Madura. Dr. J. REUTER and the author found it at Bombay, and it is reported from St. Martin just inside the tropics! It might be feared therefore that the colloidal gypsum solution would be passed into the crystallizing tables and so contaminate the salt. In fact, several samples of tropical seasalts show high percentages of sulphate. It was found, however, that the absence of *Artemia* does not mean that no pure NaCl may be produced, as other samples were practically free from sulphate. Apparently there must be another cause for this variability.

In 1929, Mr. W. GALLAGHER, Dr. D. STRAUP-COPE and the author investigated a highly alkaline lake near Marina, California at various stages of concentration. This lake is practically free from calcium and magnesium. The sulphate content of the brines proved to be exceedingly erratic, as Table III shows.

TABLE III

Cl ⁻		SO ₄ ⁼	
gm/1000	mol/1000	gm/1000	mol/1000
4.80	0.138	0.149	0.0015
20.90	0.589	0.428	0.0044
26.70	0.746	0.183	0.0019
35.35	0.996	0.624	0.0064
158.20	4.460	1.393	0.0142
135.70	3.820	6.255	0.0638

Since the work of BEIJERINCK (6) we know that sulphate may be reduced anaerobically to sulphide by bacteria and that the opposite reaction (oxidation of sulphide to sulphate) is equally "biological".

In highly buffered waters both reduction (which would tend to decrease the acidity) and oxidation (which often increases the acidity) will have very little effect upon the pH (which, in the case of the lake near Marina, proved to be > 10.0). But if the water is poorly buffered, as is the case in the marine brines of a density higher than 8° Bé, the acidity will rapidly increase with the oxidation of sulphide.

For an efficient salt-making process the reduction of the sulphate — which shows itself just below the surface as black sulphide mud — should be furthered as the experience in the "Marina" lakes has shown that sulphate may be almost quantitatively reduced!

If, however, the pan-surface is scraped and aerated, the sulphide will rapidly oxidize according to the equation given earlier in this paper.

If a sterile seawater (Cl⁻ 0.508 mol., SO₄⁼ 0.0262 mol.) is evaporated the chloride and sulphate concentration should increase proportionally until CaSO₄.2 aq precipitates and the relation between the [Cl⁻] and [SO₄⁼] may be represented by a straight line.

Figure 2 shows the actual conditions in the salt pan investigated. Here the straight line represents the theoretical increase of sulphate with chloride in a "sterile" water, the points observed are all *above* this line, which line divides the graph into an area of sulphate reduction and an area of sulphide oxidation. As the sulphates are always too high, sulphide oxidation seems to predominate which shows itself

- in the progressive decrease in pH (at 20° Bé > pH 5.0!) which tends to
- dissolve the ferrous salts, causing a decreased transmissivity to radiation (cf. figure 1).

There is no doubt that the repeated cleaning of reservoirs and tables

contributes to excessive aeration which disturbs the sulphate reduction and furthers sulphide oxidation.

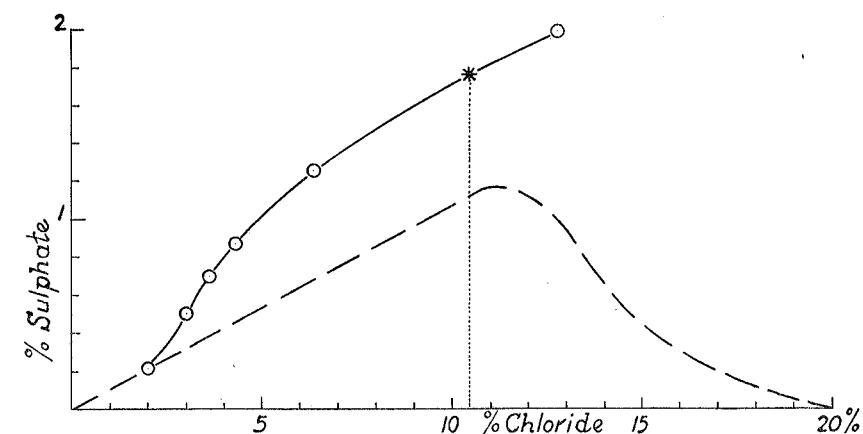


Fig. 2.

One of the tables was watched from 6—9, VII, 1937 in which time the concentration increased from 13—26° Bé with a parallel drop in pH, which actually reached a value of < 5.0 in one instance, so that not only the ferrous- but also the ferric-iron became soluble*). A sample of red salt from Hawaii, in the collection of the Botanical Laboratory at Leyden, may have originated in this way, as the soluble iron salts pass, with the mother liquor, into the crystallizing tables.

At the Saltworks of Alagamento do Horto near Setubal, Portugal which the author visited September 1936 no high acidities were observed. The salt from these ancient gardens is very pure and as the pans are almost never cleaned there is no chance for sulphide oxidation to take place.

The "redwater" is known to the salt makers of Madura, and they often speak of a "sick" pan. In most of these "sick" pans, where acidification could be shown to have taken place the sulphate reduction immediately under the surface presented an abnormal aspect. Instead of an even blackish-grey layer the profiles showed inky-black spots around partly decomposed twigs and leaves of the mangrove (api-api) which occupied the marsh previous to the construction of the salterns.

It is probable that this excessive sulphate reduction occurs at places where anaerobic cellulose-fermentation has prepared the milieu for the sulphate reducers, as laboratory experiments showed. For if we fill a stoppered bottle with (inorganic) OMELIANSKY medium + MOHR's salt, and add a strip of filter paper as a source of carbon, even in 15—20 % NaCl (after infection with mud from a saltern) rapid and almost complete cellulose-

*) In this table the H₂S concentration amounted only to 3 × 10⁻⁵ N., while in the same pan one reservoir at 8° Bé contained 30 × 10⁻⁵ N., another at 4.5° Bé; 53 × 10⁻⁵ N. H₂S.

desintegration sets in, followed by a marked sulphate reduction, as shown by the formation of hydrotroilite. Aeration of this culture will give rise to both aerobic thio-bacteria and to iron-bacteria.

It may be that during the cellulose fermentation organic acids and their salts are liberated, which compounds serve as a carbon source for the sulphate reducers.

Discussion.

OHLE (17) states: "dasz die in der Natur gefundenen besonders niedrigen pH Werte (pH < 5) stets von Schwefelsäure oder hydrolytisch dissoziierten Sulfaten abhängig sind". This statement seems extreme — especially in view of the cases where acidity originates by base-exchange. Still sulphuric acid appears as a very common cause of extreme acidity of natural waters.

In the three cases mentioned in this paper the acidity of the water of Kawah Tjiwedéh is apparently caused by volcanic sulphuric acid while the acidity of the salterns at Madura are caused by the, probably bacterial, oxidation of sulphides. Remains the case of Lake Tyrrell. According to the analysis, very little calcium was present, the original brine must have been very weakly buffered. A week or so before our visit the salt was harvested by scraping and the underlying sulphide was aerated. It seems reasonable that also in this case this process is bacterial in origin. It may be that in this case, like in the claypit investigated by OHLE, (the waters of which showed an acidity pH = 3.5) sulphide minerals present in the clay and other than the bacterial hydrotroilite contributed to the formation of the acid. OHLE, however, and most other authors do not mention the bacterial activity concomitant with the sulphide oxidation which, to them, seems a purely geochemical reaction.

It seems to me very likely that these oxidations are, at least partly, caused by biological processes.

It appears that the solar process of salt manufacture is a biological process. Both the disappearance of the calcium carbonate and the gypsum show themselves as influenced by the activity of living organisms.

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*) The papers marked with an asterisk contain extensive literature-surveys.