

A DISCUSSION OF THE SOLUTION OF LIMESTONE BY SULFURIC ACID AND ITS IMPORTANCE IN AUSTRALIAN CAVES

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INTRODUCTION

In most karst systems the excavation of limestone by the action of sulfuric acid has been neglected because it is the minor corrosive agent. The major cavity excavator is the acid produced by the solution of carbon dioxide in water ("carbonic acid"). During the two last decades a number of caves have been identified where sulfuric acid is making the major contribution to their present solutional enlargement. Cavern development by sulfuric acid can be divided into three general categories:

Type 1-solution Waters containing sulfuric acid dissolve the limestone and the products are removed as carbon dioxide into the cave atmosphere and as ions in the cave water.

This type of sulfuric acid action is usually associated with acid mine drainage and was first discussed (Howard, 1960 and Morehouse, 1968) in papers on the speleogenesis of the Dubuque Caves, Iowa, USA. The caves were discovered during intensive mining of the district for lead and zinc sulfides. Type 1 sulfuric acid dissolution of limestone is also taking place at the Ok Tedi Gold mine in Papua New Guinea. Waters seeping from mineralised skarns of pyrite and chalcopyrite are extremely acid (average pH of 2.3) and flow directly onto the Darai limestone, eroding it. Drilling has produced large cavities in the limestone adjacent to the skarns. There are numerous examples of this type of sulfuric acid attack on limestone recorded in the international speleological literature.

Type 2-replacement-solution This is the action of sulfuric acid on the limestone replacing it with gypsum and then subsequently the gypsum is dissolved to form a cavity.

The first record of *in situ* replacement of limestone by gypsum was made by White and Pohl, 1965 where in order to explain the morphology of the gypsum deposits encountered in Mammoth Cave, Kentucky, USA they postulated gypsum replacement of limestone in the cave walls by attack of acidic sulfate solutions. These authors did not extend their discussion to the implications of the above observation on the solution of limestone and the development of caves.

Egemeier, 1973 first introduced the concept of the replacement of calcium carbonate by gypsum and then the subsequent solution of the gypsum to create caverns. Egemeier developed his theory from a detailed examination of the Kane Caves, Big Horn Basin, Wyoming, USA. The chemical analytical data in Egemeier's thesis (Egemeier, 1973) and the resulting paper (Egemeier, 1981) are still the most detailed and comprehensive of any study of any cave where replacement-solution is taking place. In his discussion he produces convincing morphological evidence for cavern development by replacement-solution. We (James and White in preparation) have carried out additional experiments and our results confirm that replacement-solution is currently occurring in Lower Kane Cave and Hellespont Cave.

The cave in the Cave and Basin Hot Springs, National Park on Sulphur Mountain, Banff, Canada has been made by a thermal spring which first produced an enormous tufa deposit. Then as the dominant chemical characteristics of the spring changed from carbonate to sulfate and hydrogen sulfide, erosion of the tufa commenced. The sulfuric acid produced by oxidation of hydrogen sulfide is replacing the calcium carbonate of the tufa with gypsum. The gypsum is dissolving and a cave is growing in the tufa. Cesspool cave, Virginia, USA (Hubbard *et al.*, 1986) is of similar origin.

Cueva del Azufre in Tabasco, Mexico (Azufre is Spanish for sulfur) (Pisarowicz, 1988) is certainly the most active and thus the most unpleasant sulfuric acid cave yet recorded. The water flowing out of the cave is milky white with colloidal sulfur. Inside the cave the white gypsum covered cave walls are mottled bright yellow from sulfur crystals. The water dripping from the walls has a pH of 1 resulting in the disintegration of caving overalls and acid burnt cavers. To add further to the discomfort of the cavers the temperature of the cave water is 30°C.

The above examples are active caves where replacement-solution is currently taking place and when discovered were regarded as rare, however, already other examples have been recorded in Italy and the USSR. Once the active replacement-solution had been observed to be occurring in these caves, numerous investigators began to find evidence that many other caves could have had an episode of enlargement by sulfuric acid erosion.

The most studied examples are the caves of the Guadalupe Mountains, New Mexico, USA. The best known cave is Carlsbad Caverns and the evidence for an episode of sulfuric acid attack is extensive - a review can be

found in Hill, 1987. I will only quote one piece of the morphological evidence for limestone replacement by gypsum as presented by Queen *et al.*, 1977.

"Gypsum blocks in Carlsbad Caverns and Cottonwood Cave may be found to display all petrographic textures found in the surrounding carbonates, travertine, pisolites, fossils, breccias, bedding and primary pores. Where no displacement or recrystallisation of the gypsum has occurred these textures in the gypsum may be correlated bed for bed with the carbonate. The contact of this type of gypsum with the carbonate is knife sharp."

I consider this to be conclusive evidence for replacement solution.

Salt wedging...Gypsum in its own right will enlarge caves when it crystallises in porous rock and in joints and cracks, the crystals first grow in the larger voids and then force their way into the smaller ones. The forces exerted by the growing gypsum crystals are great and can exceed the mechanical strength of the rock causing it to fracture.

This process is occurring in many caves; if the rock is competent little wedging takes place, the gypsum forms as a crust which periodically falls to the floor as a gypsum snow. An example of such a deposit can be found in Mamo Kananda, Muller Range, PNG these cave passages tend to be small and cavern enlargement is minimal. However, if the limestone is porous then sands consisting of limestone and gypsum and fallen boulders are the result of wall rock breakdown. Such breakdown deposits are frequently encountered in the higher dry levels of the Zongolica Caves, Chilchotla, Oaxaca, Mexico where the resulting caverns are frequently very large.

AUSTRALIAN EXAMPLES

Type 1 solution There are as yet no recorded Australian examples of this type of sulfuric acid attack. However, there is potential for Type 1 caves to form. There are a number of areas where sulfide mineralisation is associated with limestone, for example Cooleman, Wombeyan and Cleifden in NSW. Caves known to be close to such mineralisation should be examined for evidence of sulfuric acid weathering.

Type 2. replacement-solution Again there are no recorded Australian examples of replacement-solution either currently active caves or of caves that may have formed by sulfuric acid action in the past.

Type 3 salt wedging Enlargement of caves by gypsum crystal wedging definitely occurs in many Australian Caves. Australia is the second driest continent and has many arid and semi-arid karst areas. There have been periods of gypsum wedging in the caves of the Nullarbor although at present any action due to gypsum is eclipsed by halite wedging.

It is clear from this brief survey that it is unlikely that there are going to be Australian caves where sulfuric acid corrosion is greater than "carbonic acid" corrosion. However there is often subtle corrosion from sulfuric acid taking place in caves and if there is adequate analytical data available for the cave waters then it is possible to calculate its contribution to the total erosion.

INDICATORS OF SULFURIC ACID CORROSION

There are two main indicators that sulfuric acid has been or is active in caves. Sulfate speleothems in the cave and sulfate in the cave waters.

Sulfate minerals in the caves

The presence calcium sulfate-2-water as gypsum or selenite in the cave may indicate that there has been sulfuric acid attack on limestone.

- * In Australian caves gypsum is the second most common secondary mineral; calcite being the first.
- * Gypsum can be found in caves at all latitudes and has been recorded as being present in caves from Far North Queensland to Tasmania.
- * In caves of all altitudes; the highest Australian gypsum is to be found Yarrangobilly Caves in the Snowy Mountains and Anna Kananda in Tasmania, the lowest a few metres above sea level in Pannikin Plain cave on the Nullarbor Plain.
- * In caves from areas with a wide range of precipitation; gypsum is found in very wet caves such as Herberts' Pot, Tasmania to extremely dry caves below the desert. However, it is in the caves below the desert that gypsum is most frequently found.

Forms of gypsum. There are almost as many varieties of gypsum speleothems as there are of calcite. The various morphologies of gypsum and selenite deposits found in caves are classified and described in Hill and Forti, 1986.

The following general observations can be made about gypsum speleothems

- * Gypsum speleothems in most caves do not occur with calcite; gypsum flowers the classical example of evaporite speleothems are usually pure gypsum although they may contain occluded detrital materials.
- * Massive gypsum crystals and selenite grow from muds in places where there is no observable calcium carbonate or sulfate source.
- * Gypsum speleothems are fast growing and ephemeral.

Conditions for gypsum growth The most important conditions for gypsum growth are reduced humidity either by the cave atmosphere being dry or by the gypsum carrying solutions being evaporated by strong draughts.

Sulfate in the cave waters

The other indicator of sulfuric acid attack on limestone is sulfate in the cave waters. All cave waters contain some sulfate, unfortunately until recently it has been difficult to analyse for sulfate and thus has often been omitted from karst water analyses.

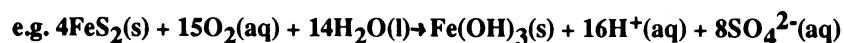
SOURCES OF SULFATE

If there is gypsum in the cave or sulfate in the karst waters then it can have come from one or more of the following sources.

Solution of sulfate deposits In the arid and semi-arid regions of Australia the gypsum in the caves may be derived from the mineral being present on the surface or in rock strata and dissolving in seepage water and reprecipitating on entry to the caves. Limestones may contain deposits of both anhydrite and gypsum if these are directly in the path of descending meteoric waters, solution of the sulfate will take place and cause a cavity to form.

Sea-water and sulfate thermal and connate waters The caves of the Nullarbor have been invaded by Sea-water and the sulfate levels are very high. Many Australian groundwaters have a high sulfate content.

The oxidation of sulfides Sulfides are sources of reduced sulfur and can thus be oxidised to sulfuric acid.



Pyrite and chalcopyrite are the only commonly occurring sulfides that can generate acid. Other sulfides can relocate acid (relocation implies separation of the two reactions either by space or time: that is the overall reaction has no net generation of acid. Most Australian limestones contain some pyrite and this reaction will be occurring to some extent in any cave that is in a limestone that contains pyrite.

Hydrogen sulfide is produced by acid attack on sulfides and by the decomposition of organic materials containing sulfur and by bacterial sulfate reduction. When organics or bacteria are implicated in the production of hydrogen sulfide in acidic conditions carbon dioxide will also be produced. Most of the H_2S formation on earth is due to the bacteria of the genera *Desulfovibrio*, *Desulfotomaculum* and *Desulfomonas*. These bacteria are widely distributed in caves and in the soil above caves, thus a component of the erosion will be due to sulfuric acid in all caves where the carbon dioxide comes from organic sources. During the oxidation of hydrogen sulfide there is no net acid production however a weak acid is converted to a strong acid.

Elemental sulfur oxidation Oxidation of sulfur produces sulfuric acid however native sulfur is rare in caves and will not be discussed here.

Acid rain A major component of acid rain is sulfuric acid, this when it falls on karst can cause considerable dissolution of the limestone.

In many parts of Europe and North America cavers are claiming to be able to observe the effects of acid rain in caves. A number of studies are in progress in order to quantify its contribution to the development of caverns and the solution of speleothems. Acid rain is unlikely to become a problem in Australian karst areas.

CALCULATIONS ON THE AMOUNT OF SULFURIC ACID CORROSION OF KARST

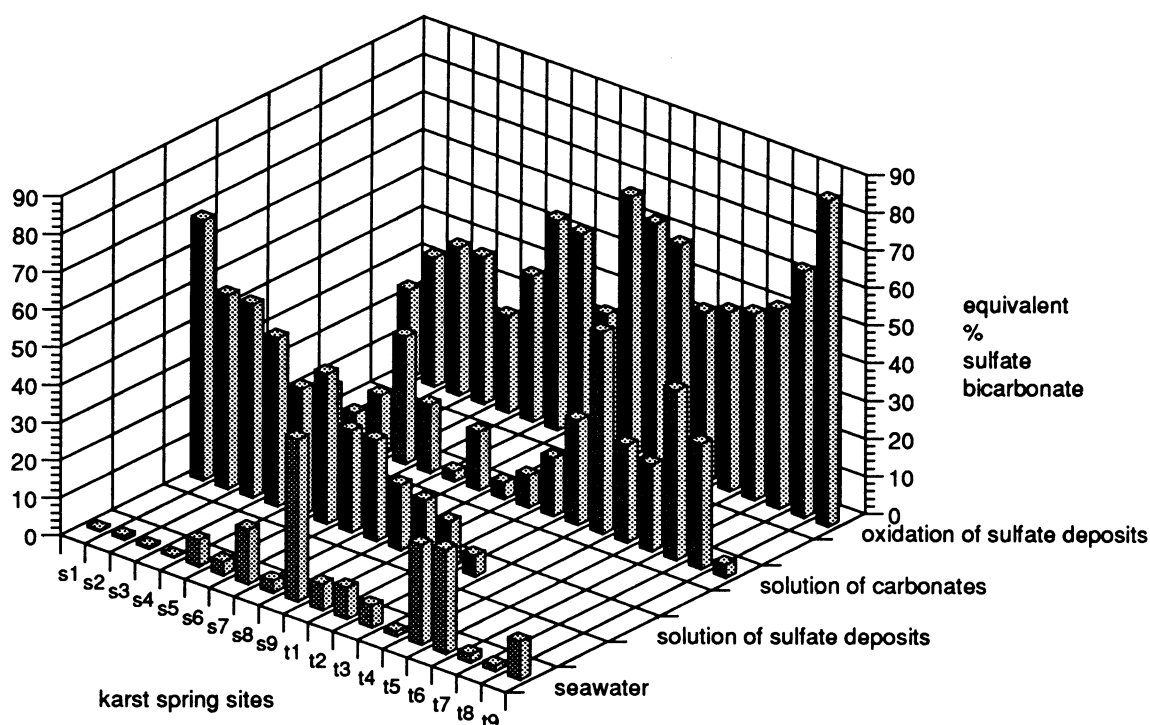


Figure 1....The origins of sulfate in various USSR karst waters (Durov, 1956).

The first literature contribution quantifying the contribution from various sulfate sources was a paper by Durov, 1956. This paper fortunately has been translated from Russian and reprinted in the Cave Geology series of the National Speleological Society. It has suffered in translation and unfortunately the original chemical data has been omitted. The conclusions presented in Durov, 1956 are shown in Figure 1; of the 19 examined cases.

- * 11 of them have a predominance of the products of the oxidation of sulfides
- * In 7 cases dissolving gypsum does not merit any attention as a source of dissolved salts.
- * In 6 out of the twelve cases where a component can be attributed to dissolving of gypsum the products of the zone of oxidation exceed that due to dissolving gypsum.
- * In 17 cases, the overwhelming majority the action of sulfuric acid is significantly greater than that of carbonic acid.

Since the Durov 1956 paper no one had considered the sulfate content of karst waters as an indicator of the sulfuric acid reaction. Durov's calculations were complex and involved the use of other ions present in karst waters. If the chemistry of the input and spring waters is known and provided the chemical analysis does not show any influence of sea-water, other saline waters or solution of calcium sulfate deposits. A simple calculation can be carried out to estimate the extent of sulfuric attack on the limestone.

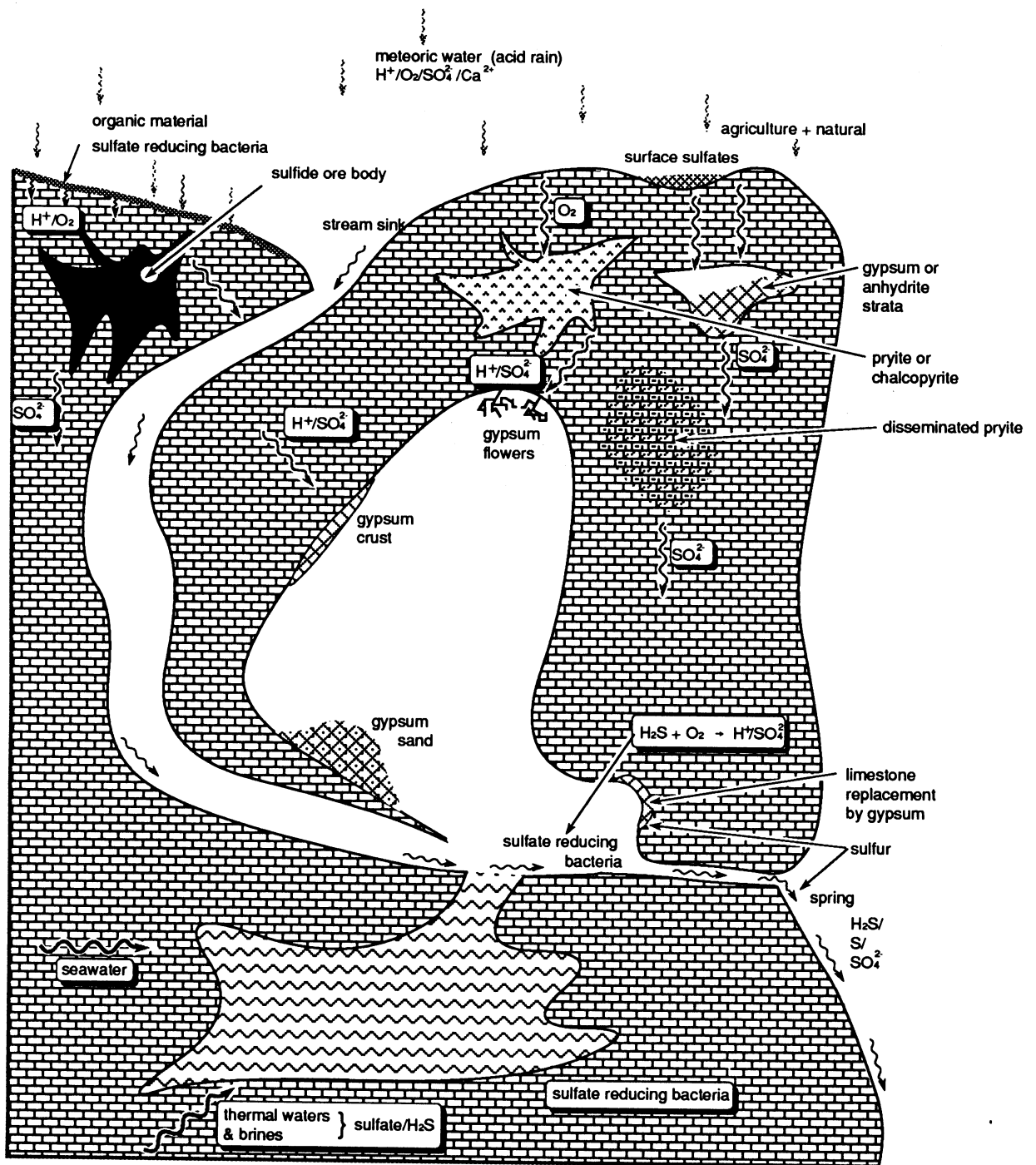
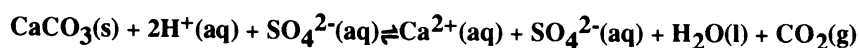


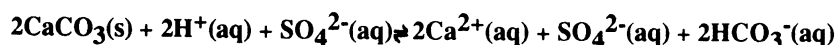
Figure 2...Sulfates and sulfuric acid in caves

There are two reactions of sulfuric acid with limestone.

(1) EXCESS SULFURIC ACID



(2) EXCESS CALCIUM CARBONATE



When calcium carbonate is treated with excess sulfuric acid the first reaction takes place. From this equation it can be observed that one 1 mole of $\text{H}_2\text{SO}_4(\text{aq})$ will dissolve 1 mole of $\text{CaCO}_3(\text{s})$.

When calcium carbonate is in excess...the situation in the cave....the reaction is represented by the second equation. It should be noted that one mole of sulfuric acid will now dissolve two moles of calcium carbonate. This reaction can be used to calculate the extent of sulfuric acid corrosion.

For example Harvy Creek Cave Spring (Ok Tedi, PNG) waters contain 112 mg L^{-1} of calcium carbonate and 20 mg L^{-1} of SO_4^{2-} . Using the relationship in equation (2), calculations show that some 30-40% of the solution has taken place by oxidation of sulfides. This is not surprising as the cave waters are known to collect in and drain through pyrite skarns, a small component of this will be derived from the oxidation of reduced organic sulfur. Definitely no gypsum solution as the average annual rainfall is 8.3 m. and definitely no sea-water the spring is at an altitude of 1800 m.

Doing similar calculations for the Bungonia Efflux waters I get an 8% contribution from sulfuric acid corrosion. In all areas where there is decaying organic material there will be always be a small proportion of sulfuric acid weathering. This should be considered a normal contribution and to be present in all karst waters generated by organically produced carbon dioxide.

Preliminary calculations on the Nullarbor cave waters indicate that most of the sulfate comes from sea-water or connate waters and there will be a small component from calcium sulfate-2-water from the surface of the plain and within the limestone. At present there is no sulfate component that can be identified as coming from the oxidation of sulfides either mineral or organic.

CONCLUDING REMARKS

Figure 2 summarises the discussion in this paper on sulfuric acid and sulfates in caves. It is clear that there is cavern development due to sulfuric acid in Australia but in the cases where it can be identified its effect is small when compared with that due to carbonic acid.

There is a need to examine Australian caving areas for corrosion by sulfuric acid, both present and past. Wherever karst waters are analysed it should be routine to measure the following; calcium, magnesium, sodium, potassium, hydrogencarbonate, chloride and sulfate. The pH should be measured on a calibrated pH meter to 2 decimal places. These are the essential parameters needed to calculate the relative importance of corrosion by sulfuric acid to that by carbonic acid.

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