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The reducibility of sulphuric acid and sulphate in aqueous solution (translated from German)

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July 1990

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Translation from German

THE REDUCIBILITY OF SULPHURIC ACID AND SULPHATE IN AQUEOUS SOLUTION

(Über die Reduzierbarkeit von Schwefelsäure und Sulfat
in wäßriger Lösung)

by Rolf Grauer
Paul Scherrer Institute

July 1990

SUMMARY

In connection with the Swedish project for the final storage of spent fuel elements it was necessary to assess whether dissolved sulphate can corrode the copper canister without the intervention of sulphate-reducing bacteria. A simple reaction between copper and sulphate is thermodynamically impossible. On the other hand, copper can react to give copper sulphide if an additional electron donor such as iron(II) is available. Because little specific information is available about this subject the problem was extended to the much more general question of the reducibility of sulphur(VI) in dilute aqueous solution.

It is a part of the general knowledge of chemistry, and there is also unanimity about it in the geochemical literature, that purely chemical reduction of sulphate does not take place in dilute solution at temperatures below 100°C. This fact is, however, poorly documented and it was therefore necessary to substantiate it by drawing on numerous individual findings from different areas of pure and applied chemistry.

In experiments on the reduction of sulphates under hydrothermal conditions a reaction only takes place at temperatures above 275-300°C. In the case of the action of sulphuric acid on metals its oxidising action becomes perceptible only at acid concentrations over 45-50%.

From experiments on the cathodic reduction of 74% sulphuric acid it is found that the formation of hydrogen sulphide and elementary sulphur starts, depending on the current density, at 50-130°C, and polarographic measurements lead to the conclusion that the reducible species is not the hydrogen sulphate ion but molecular sulphuric acid. In dilute solutions the latter's concentration is vanishingly small, however.

From corrosion chemistry the resistance of copper to oxygen-free sulphuric acid up to a concentration of 60% is well-known. Copper is also used as a pipe material in the production of iron(II) sulphate; it is thus stable even in the presence of the electron donor iron(II). Although base metals such as iron and zinc can, according to the thermodynamics, reduce sulphate in aqueous solution, such cases are unknown despite the widespread use of these materials.

Numerous processes in industrial electrochemistry take place in sulphuric-acid or sulphate electrolytes, such as the electrochemical extraction and refining of metals, electrochemical deposition of metals and the anodic oxidation of aluminium. Cathodic sulphate reduction would reduce the quality of the products of such processes and there would also be health and safety consequences because of the formation of hydrogen sulphide.

The reversible metal/metal-sulphate electrodes of lead and cadmium are unstable relative to the corresponding metal sulphide. Nevertheless the reversible lead sulphate electrode functions in the starter-battery of 450 million vehicles and in

stationary batteries without failing due to sulphide formation. In the Weston cell, which is used as a secondary standard for the electrical voltage, the cadmium-sulphate electrode remains stable for decades, such that these cells can be calibrated.

Finally, sulphuric acid and sulphate solutions are widely used in basic electrochemical research as inert supporting electrolytes. Their instability would make exact and reproducible measurements impossible.

All these facts confirm that sulphur(VI) in dilute solution is completely inert towards chemical reducing agents and also to cathodic reduction. Thus corrosion of copper by sulphate under final-storage conditions and in the absence of sulphate reducing bacteria can be ruled out with a probability verging on certainty.

1. INTRODUCTION

In the Swedish project for the final storage of spent fuel elements it is planned to weld the used fuel rods into a thick-walled copper canister. As part of the container evaluation the corrosion behaviour of copper has been discussed exhaustively [65, 66].

Under reducing conditions such as are to be expected in a final repository copper is thermodynamically stable[1]:

$$2\ Cu + H_2O \rightleftharpoons Cu_2O + H_2 \qquad (1)$$
$$(\Delta G^\circ = +90.83\ kJ;\ \log K_p = -15.91)$$
$$Cu + 2\ H^+ \rightleftharpoons Cu^{2+} + H_2 \qquad (1a)$$
$$(\Delta G^\circ = +65.48\ kJ;\ \log K_p = -11.47)$$

In sulphide-containing waters, however, corrosion takes place with the evolution of hydrogen:

$$2\ Cu + HS^- + H^+ \rightleftharpoons Cu_2S + H_2 \qquad (2)$$
$$(\Delta G^\circ = -98.28\ kJ;\ \log K_p = -17.22)$$

Here, it is assumed that the rate of this reaction is determined by the rate of supply of the hydrogensulphide [65].

Since sulphates are transformed into hydrogen sulphide by sulphate-reducing bacteria the possibility exists that a proportion of the sulphate present in the water or in the backfill can act indirectly as an oxidising agent [48; 65, App. C]. In this connection the question has been asked whether a purely chemical reduction of sulphate is also possible. The sulphate contents of groundwaters lie in the range 0.1-1 mmol/litre [63] and as the upper limit - except in the case of specific saline subterranean waters - saturation with gypsum can be assumed (15 mmol/litre). If corrosion reactions involving the direct participation of sulphate as oxidising agent were possible this would have serious consequences for the integrity of metallic canisters.

It is in fact part of the chemist's elementary general knowledge that sulphates are not reducible in dilue aqueous solutions. This fact is, however, poorly documented and many chemical text-books do not refer to it explicitly - because it is assumed to be obvious. Charlot [11] emphasises in his text-book the redox-inactive behaviour of sulphate solutions, and Mahan [43] states:

> "Hot concentrated sulfuric acid is an oxidising agent, and will dissolve metals like copper. In diluted solutions, however, the oxidising properties associated with the sulfate group are virtually negligible."

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[1] The stability of copper in oxygen-free solutions is queried by Hultquist et al [33]. For this reason it is once more necessary to prove that the laws of thermodynamics are also valid for corrosion reactions [16, 62].

Schwarzenbach [61] writes:

> "Sulphate ions are also not reducing agents and have no appreciable oxidising effects. By contrast, concentrated sulphuric acid is a quite pronounced oxidising agent."

All these statements are vague and form a poor basis for reliable argumentation.

2.STATEMENT OF THE PROBLEM AND THE STRATEGY FOR SOLVING IT

The task set is to clarify, on the basis of the existing literature whether the corrosion of copper in aqueous solution is possible by the reduction of sulphate without the involvement of sulphate-reducing bacteria.

It is not to be expected that sufficient information exists to answer this very specific question. The subject must therefore be broadened. On the widest possible basis the question to be clarified is whether sulphuric acid and sulphate can be reduced purely chemically in dilute aqueous solution (eg < 1 M) at temperatures up to 100°C.

The feasibility of such a reaction would be demonstrated by a single solid positive finding. By contrast, proof of the redox stability of aqueous sulphate solutions is in the strict sense impossible because it cannot be demonstrated using the fundamental arguments of thermodynamics. All negative results have only the status of observations whose validity can be overturned at any time by a contrary finding[2].

In order nevertheless to arrive at a high reliability of the conclusion it is necessary to support the argumentation broadly and to call upon findings from the largest possible number and most widely different sub-fields of chemistry.

Because kinetically inhibited redox reactions (eg reductions by hydrogen) can be catalysed by metal surfaces attention must above all be directed towards electrochemical reactions in sulphate electrolytes. The information about these is diverse; it comes from industrial electrochemistry, from the battery industry, from corrosion chemistry and finally from basic research in electrochemistry.

In comparison with this extensive reservoir of information, publications on experiments specifically concerned with the reduction of sulphuric acid and sulphates are relatively rare, and geochemical findings about the behaviour of sulphate are, considered separately, not very persuasive.

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[2] The observation "All swans are white" was confirmed by innumerable examples and was incontestable for centuries. After the discovery of South America (and the black-necked swan living there) its validity could be doubted. After the discovery of the Australian continent (and the black swan) it was falsified, (cf. [55]).

3. THERMODYNAMICS OF CORROSION BY SULPHATE

The values of the Gibbs free energies of formation have been taken from the book by Brookins [9]; these are mainly data from the National Bureau of Standards. A few figures come from the compilation in [63].

In the potential-pH diagram of the sulphur/water redox-system only HSO_4^-/SO_4^{2-}, S° and $H_2S/HS^-/S^{2-}$ have a stability region (Fig 1.). All the other species are metastable. The stability region of elementary sulphur becomes smaller with decreasing concentration of the sulphur species and disappears at $[S]_{tot} \approx 10^{-6}$.

Fig 1 shows that for base metals such as iron, nickel and zinc corrosion by sulphate is thermodynamically possible, so for example

$$SO_4^{2-} + 4\ Fe + 8\ H^+ \rightleftarrows FeS + 3\ Fe^{2+} + 4\ H_2O \qquad (3)$$

$$(\Delta G^\circ = -541.37\ kJ;\ \log K = +94.84)$$

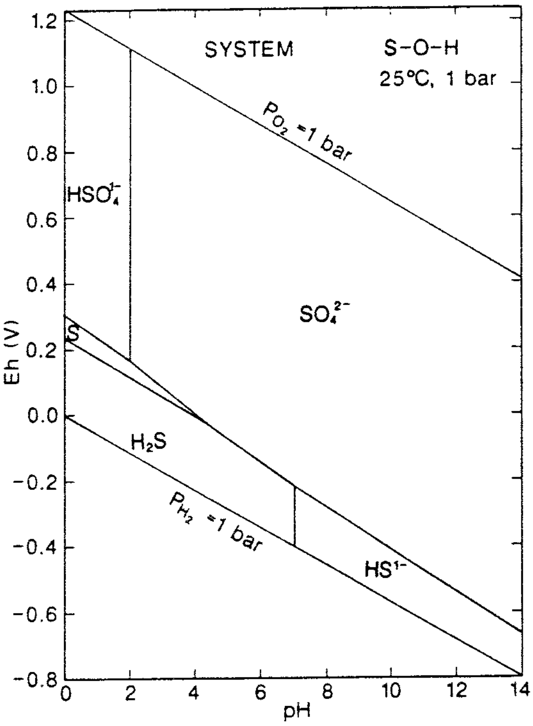

Fig 1.
Potential-pH diagram for the system sulphur/water $[S]_{tot} = 10^{-3}M$ [9].

Fig 2 shows the potential-pH diagram for the system $Cu/S/H_2O$ with the inclusion of carbon dioxide. The stability region of elementary copper is much smaller than it is in the diagram for the system Cu/H_2O (Fig 3), and Fig 2 shows that copper(O) can be formed both by reduction of the oxide and by the oxidation of chalcocite (Cu_2S).

The direct oxidation of copper by sulphate in accordance with

$$SO_4^{2-} + 8\ Cu + 2\ H^+ \rightleftharpoons Cu_2S + 3\ Cu_2O + 4\ H_2O \qquad (4)$$

($\Delta G° = -17.91$ kJ; $\log K = +3.14$)

is impossible in the pH range of natural waters: at pH 7 we have $[SO_4^{2-}] = 10^{+10.86}$.

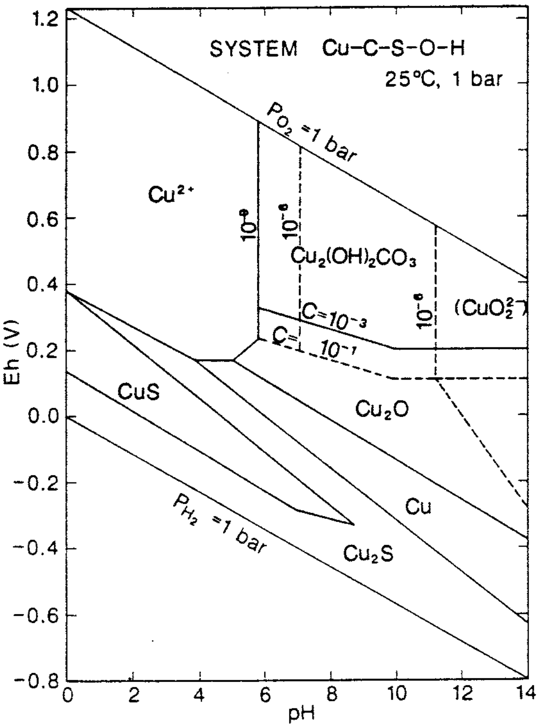

Fig 2.
Potential-pH diagram for the system $Cu/S/C/H_2O$.
$[Cu^{2+}] = 10^{-6}$ M; $[S]_{tot} = 10^{-3}$ M; $[C]_{tot} = 0.1$ or 10^{-3} M [9].

In the presence of additional electron donors such as iron(II), however, the formation of chalcocite is in principle possible, if the solid phase of iron (III) is assumed to be hematite:

$$SO_4^{2-} + 2\ Cu + 6\ Fe^{2+} + 5\ H_2O \rightleftharpoons Cu_2S + 3\ Fe_2O_3 + 10\ H^+ \qquad (5)$$

($\Delta G° = +91.17$ kJ; $\log K = -15.97$)

For pH = 7 and $[Fe^{2+}] = 10^{-5}$, $[SO_4^{2-}]$ becomes 10^{-24}.

If, however, one assumes that the system is saturated with amorphous iron(III) hydroxide (or that this compound occurs as the primary reaction product) one arrives at a different conclusion:

$$SO_4^{2-} + 2\ Cu + 6\ Fe^{2+} + 14\ H_2O \rightleftharpoons Cu_2S + 6\ Fe(OH)_3 + 10\ H^+ \qquad (6)$$

($\Delta G° = +273.42$ kJ; $\log K = -47.90$)

With the same assumptions as above $[SO_4^{2-}]$ now becomes $10^{7.9}$. At pH 8, however, $[SO_4^{2-}] = 10^{-2.1}$.

The large stoichiometric coefficients are responsible for the fact that the calculated equilibrium concentration shifts drastically for trivial changes in pH.

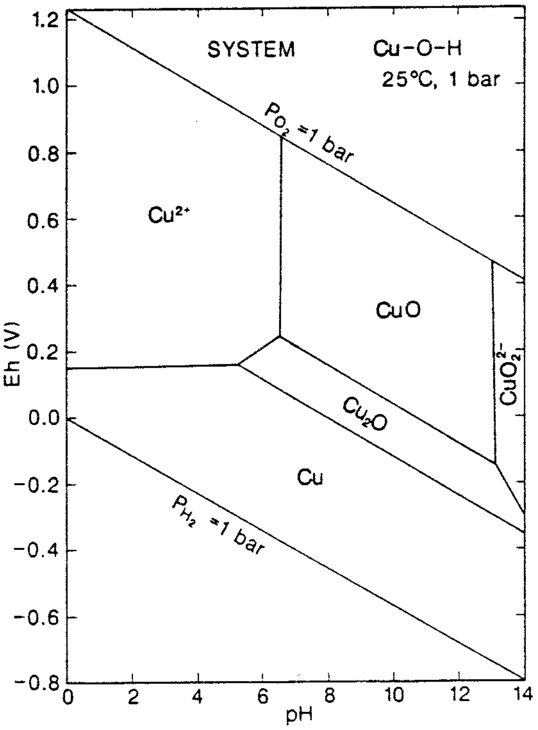

Fig 3.
Potential-pH diagram for the system copper/water.
$[Cu^{2+}] = 10^{-6}$ M [9].

4. GEOCHEMICAL INFORMATION ABOUT THE REDOX STABILITY OF SULPHATE

In the geochemical literature there appears to be unanimity about the fact that sulphate reduction in the hydrosphere and in sediments takes place exclusively bacterially and that an inorganic reaction is not possible. This is not always formulated explicitly, however. Nevertheless we have found the following statements:

> "There is no known purely chemical mechanism for the reduction of sulfate by organic matter at normal earth temperatures and pressures, so that microorganisms are completely responsible for this process." [85]

> "The rates of nonbiological reduction of SO_4^{2-} to H_2S by geologically reasonable reducing agents at room

> temperature are immeasurably slow." [7]
>
> "Under inorganic conditions many ions, notably sulfate, may persist metastably during long periods of time, but the presence of organic material and the accompanying bacteria almost guarantees approach to equilibrium, as denoted by the by the measured potentials." [17]

An unequivocal, sound proof of such statements based on geochemical findings would probably be difficult because frequently the boundary conditions are not sufficiently well-known or because a bacterial reduction of sulphate can never be ruled out with certainty. Therefore we shall draw no conclusion here from the well-documented situation of native copper [45].

In [29] the stability of siderite in sulphate-containing anaerobic waters is discussed:

$$SO_4^{2-} + 9\ FeCO_3 + 8\ H_2O \rightleftharpoons FeS + 4\ Fe_2O_3 + 9\ HCO_3^- + 7\ H^+ \qquad (7)$$

($\Delta G° = +292.09$ kJ; $\log K = -51.17$)

For typical hydrogen carbonate concentrations (1 mM) and pHs (7) of natural waters, equilibrium concentrations of sulphate are extremely low - of the order of 10^{-25}. One would thus expect siderite to be unstable in practically all waters and that the transformation products iron sulphide (or pyrite) and hematite would be found on siderite.

If it is assumed that the primary reaction-product is amorphous iron(III) hydroxide, which is only dehydrated in a subsequent reaction, then contrary conclusions emerge:

$$SO_4^{2-} + 9\ FeCO_3 + 20\ H_2O \rightleftharpoons FeS + 8\ Fe(OH)_3 + 9\ HCO_3^- + 7\ H^+ \qquad (8)$$

($\Delta G° = +535.09$ kJ; $\log K = -93.75$)

For the concentration conditions stated above the equilibrium concentration of sulphate now becomes, at 10^{-18} M, unrealistically high.

This example shows with complete clarity that it is extremely hazardous to assess stability conditions in the geosphere solely on the basis of formal thermodynamic considerations.

5. EXPERIMENTS ON THE REDUCIBILITY OF SULPHURIC ACID AND SULPHATE

5.1 Hydrothermal experiments

Experiments on the reduction of solutions of zinc sulphate with hydrogen in autoclaves showed that the formation of detectable amounts of zinc sulphide begins, at hydrogen pressures of 8-190 bar, only at temperatures of 275°C [44]. The experiments lasted 48-140 hours.

Toland [67] reported on experiments on the oxidation or organic compounds in aqueous solutions of sulphate (ca 0.5 M) in the temperature range 315-350°C. The major part of sulphate such as methane, cyclohexane and xylenes reacted over a period of about an hour when the reaction system also contained hydrogen sulphide. The catalytic action of the hydrogen sulphide is mentioned particularly and it is also stated: "Below about 300°C sulfate reduction becomes extremely slow."

Oxidation experiments with sulphate solutions <u>without</u> hydrogen sulphide are not described in detail. From the context, however, it emerges that up to 350°C no reaction took place.

5.2 The oxidising action of sulphuric acid on metals

Dilute sulphuric acid behaves towards the common industrial metals as a non-oxidising acid. The temperature and concentration conditions under which an oxidising action begins to take place have not been precisely determined. The older literature contains the following individual results:

<u>Copper</u>: The oxidising effect of the acid becomes appreciable at concentrations over 12.5 M (74%) [22]. In concentrated acid (96-98%) the copper reacts slowly even at 0°C to give copper sulphate and copper(I) sulphide, sulphur dioxide also being formed.

<u>Iron</u>: The reduction of sulphuric acid by iron starts to take place according to two different sources at acid concentrations of 7.1 and 9.4 M (50 and 62% respectively) [21].

<u>Tin</u>: At room temperature a slight evolution of hydrogen sulphide and deposition of sulphur are observed at concentrations above 10.3 M (65%). In the temperature range 110-130°C the acid begins to decompose at concentrations of 6-7 M (44-50%) [20].

<u>Lead</u> is used as a corrosion-resistant material in the sulphuric acid industry up to acid concentrations of 13.5 M (78%) and at temperatures up to 110°C [72].

If one summarizes these individual findings it is seen that the oxidising action of sulphuric acid on metals starts at concentrations above 6-7 M (45-50%).

5.3 Experiments on the cathodic reduction of sulphuric acid and sulphate

Bancroft and Magoffin [3] have electrolysed 12.5 M (74%) sulphuric acid at various temperatures and identified the cathodic reaction products. The original paper does not give data on current densities or state the methods used to identify the products. At a platinised platinum wire (presumably at a relatively high current-density) only hydrogen is generated up to 50°C; at 80°C hydrogen sulphide is also formed. At a platinum foil (presumably at a lower current-density) reduction of the sulphuric acid started only at 130°C. Without stating the experimental details the same authors state in a later paper: "Sodium sulfate and ammonium sulfate cannot be reduced at any concentrations and temperatures that can be reached in open vessels" [4]. Nor could dissolved sodium sulphate be reduced by hydrogen in the presence of platinum [3]. The mixture had, over 6 months, been fused into glass.

Gehrke [18] succeeded with an unusual experimental set-up in producing hydrogen sulphide and elementary sulphur from ca 3M sulphuric acid at a platinum cathode. The cell voltage was 110 V (!) and the wire cathode, in the form of a point electrode, was only wetted to a very small extent. In addition to the high voltage and the unmonitored high current-density it is possible that a local rise in temperature also contributed to the phenomena observed. When the acid concentration was reduced to 0.7 M no sulphate reduction was observed even over several days.

5.4 Polarographic investigations of the cathodic behaviour of sulphuric acid

Beck [6] has investigated the cathodic behaviour of sulphuric acid in the concentration range from 50 to 100% polarographically at the dropping mercury electrode. Fig 4 shows the current/potential curves. If the acid concentration is raised from 50% to 85% the steep rise in the current shifts only slowly to more positive potentials. In 90% acid a transition is observed and at an acid concentration of 95% the rise in the current takes place at a considerably higher potential.

This effect is attributed to the fact that the reduction of the sulphuric acid molecule takes place more easily than the liberation of hydrogen from the hydrogen ion. An acid concentration of 84.5% corresponds to the monohydrate which formally dissociates in accordance with the reaction

$$H_2SO_4 \cdot H_2O \rightleftharpoons H_3O^+ + HSO_4^-$$

At higher acid concentrations too little water is available for this protolysis and the amount of molecular sulphuric acid thus rises with increasing concentration.

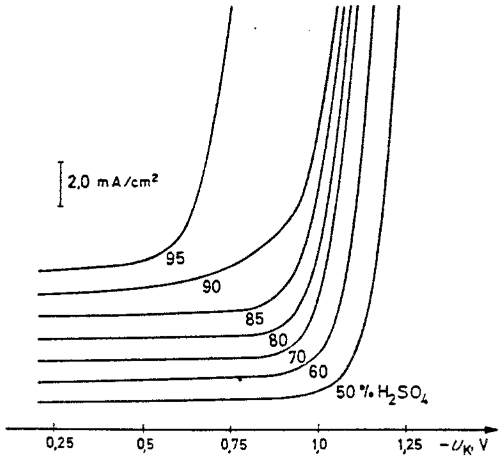

Fig 4.
Polarographic current-potential curves in 50-97% sulphuric acid (reference: saturated calomel electrode) [6].

If the water-content of the acid is below about 8% a further reduction step is observed in the -150 mV potential region (25°C) which greatly increases with decreasing water-content and with increasing temperature. It is ascribed to the reduction of solvated sulphur trioxide which is in equilibrium with molecular sulphuric acid [40]:

$$H_2SO_4 \rightleftarrows SO_3(\text{solv}) + H_2O(\text{solv})$$

Beck's investigations [6] therefore lead to the interesting result that the reduction of hexavalent sulphur only begins when the sulphuric acid is present in molecular form: it is reduced preferentially over the hydrogen ions. With a still smaller overvoltage the solvated sulphur trioxide is reduced, though it is present in significant concentrations only in highly concentrated acid (>97%).

6. THE CORROSION BEHAVIOUR OF METALS IN SULPHURIC ACID AND SULPHATE SOLUTIONS

6.1 The behaviour of copper

Copper is resistant to dilute sulphuric acid when air is excluded [14]. As the limit of use an acid concentration of 60% (9 M) at temperatures below 100°C is quoted [83]. Watts [81] reports that polished copper wires sealed into glass ampoules in de-aerated 0.5 M sulphuric acid did not change in appearance over 11 years, and that during this time the acid did not discolour either. This result is to be expected on the basis of the Gibbs free energy of Reaction (1a). With the admission of air in a cracked ampoule the metal has dissolved completely in this time.

Otsuka and Uda [51] have observed that in the case of cathodic evolution of hydrogen at copper in 0.5 M sulphuric acid copper(I) oxide is formed. This phenomenon of "cathodic corrosion" is not connected with the sulphuric acid. Under the conditions of the experiment copper hydride is formed as an intermediate and reacts to give copper(I) oxide and hydrogen. (The hydride CuH is a well-known compound [26].) The cathodic corrosion of copper is not an isolated case. On lead, too, an unstable hydride can form in water in the case of cathodic polarisation and therefore the rate of corrosion of lead increases again at low potentials [2]. This type of corrosion occurs, however, only at strongly negative potentials outside the stability range of water and can thus be ruled out for the situation in the final repository.

In Sec 3 it was pointed out that a reaction between copper and sulphate is thermodynamically possible if iron(II) is available as a further electron-donor (Reaction (5)). From the corrosion literature [14] one also finds that copper and its alloys are resistant to iron(II) sulphate solutions at pHs of 2-3 if air is excluded. Copper can be used as a pipe material in iron-sulphate production-plants up to 80°C. Corrosion in accordance with Reaction (5) thus seems to be ruled out under milder conditions.

The formerly common practice in the commercial production of copper of cementing copper ions from sulphuric acid solution with iron [68] also tells against the formation of copper sulphides in the presence of iron.

6.2 The behaviour of lead

Lead was used on a large scale as a corrosion-resistant material in the manufacture of sulphuric acid. The limits of use lie at an acid concentration of 13.5 M (78%) and a temperature of 110°C [72]. The fact that for this application lead has largely been displaced by other metals and plastics is not related to its corrosion behaviour but to its low mechanical strength and high installation costs.

In oxygen-free solutions the following two corrosion reactions are thermodynamically possible:

$$Pb + H^+ + HSO_4^- \rightleftharpoons PbSO_4 + H_2 \quad (9)$$

$(\Delta G^\circ = -57.24$ kJ: $\log K_p = +10.03)$

$$Pb + H^+ + HSO_4^- \rightleftharpoons 0.25\ PbS + 0.75\ PbSO_4 + H_2O \quad (10)$$

$(\Delta G^\circ = -115.81$ kJ: $\log K = +20.29)$

The onset of Reaction (10) limits the application of lead in sulphuric acid production.

In 90% sulphuric acid Reactions (9) and (19) proceed in parallel in the temperature range 50-90°C [23]. Lead sulphide has been identified by x-ray diffraction and by electron microscopy. For this purpose a special method of preparation was developed to image the back of the lead sulphate layers. In the case of the action of 50% (7 M) acid at 50°C lead sulphide could no longer be detected even electron-optically [23].

6.3 The behaviour of steel and iron

Iron(II) sulphate is produced industrially by dissolving iron in hot dilute sulphuric acid [69]. Nothing seems to be known about sulphate reduction (Reaction (3)) as a side-reaction.

In practical situations unalloyed steels and cast iron come into contact with sulphate-containing soils or waters. Although iron sulphides are well-known as corrosion product [25] their formation cannot be related to a purely chemical reduction of sulphate. High purity standards are set for drinking water and sulphate reduction by iron (and also by the galvanised pipes in the domestic installation) would impair the taste of the water. The corrosion of pipe materials by drinking water has been investigated intensively over the decades without any support being found for the reduction of sulphate. Papers about this are to be found in the corrosion journals.

Butler and Beynon [10] have investigated the corrosion of unalloyed steel in, among other things, boiling sulphate solutions (up to 1 M) and identified the corrosion products formed. There were no indications of the presence of iron sulphides.

7. INDUSTRIAL ELECTROCHEMICAL PROCESSES IN SULPHURIC ACID AND SULPHATE SOLUTIONS

7.1 Electrowinning and electrochemical refining of metals

Around 10% of copper and 50% of zinc are obtained by cathodic deposition from sulphate electrolytes [54, 74] (world production in 1985: copper 8.4 Mt, zinc 6.8 Mt [27]). Quantitatively smaller are electrolytic refining processes. Because, however, in this case high-purity-standards are set for the end-product it can be assumed that side-reactions such as the reduction of sulphate would attract particular attention here. Cadmium [76], cobalt [77], iron [78] and nickel [71] are refined electrochemically on a large scale. Deposition mainly takes place from sulphate baths. There are no indications of a side-reaction of the sulphate.

7.2 Electrodeposition of metals

In the electroplating industry the base metals iron, nickel, tin and zinc (among others) are deposited from sulphate electrolytes [28, 42, 70]. The sulphate contents of such baths are of the order of 1-2 moles/litre and the working temperature varies from room temperature to about 70°C. In these processes the deposition potential lies below the value of the hydrogen electrode (and thus also below the value for S(VI)/S-II)). Yet nothing is known about perturbations by sulphide formation.

As an example we shall take nickel-plating which is often used for decorative purposes so that high quality-standards are set for it. Optically perfect coatings are produced in special bright-nickel baths. Such a bath has approximately the following composition [28]:

$NiSO_4 \cdot 6H_2O$:	330 g/l
$NiCl_2 \cdot 6H_2O$:	45 g/l
Boric acid:	37 g/l
organic additives	

The pH is 3-4, the operating temperature is 60°C and the current density 50 mA/cm^2. The current efficiency is ca 95%.

If, in the deposition of bright nickel, sulphate were also reduced then the result would be the formation of black nickel sulphide. The aimed-for mirror-brightness of the coating would presumably be so strongly impaired as a result of this that the product would be unsaleable.

7.3 Anodic oxidation of aluminium

It is estimated that 5-10% of the aluminium produced (1985: 15.4 Mt [27]) is decorative reasons or as a corrosion protection coated with an anodically produced oxide layer [54]. Such layers can be produced in various electrolytes: most frequently, however, sulphuric acid is used at a concentration of about 20% (2.3 M). The current densities lie in the range 100-250 A/m^2 and the cathodes are generally made of aluminium or lead [28, 32, 75]. The open electrolytes baths stand in large sheds.

Obviously the sulphuric acid is not reduced cathodically in this process. At aluminium gaseous hydrogen sulphide would have to be liberated because aluminium does not form a stable sulphide in aqueous solution. The odour nuisance would be very great and the maximum permissible concentration in air of 10 ppm (15 mg/m^3) [73] would soon be exceeded.

8. REVERSIBLE SULPHATE ELECTRODES

8.1 The lead/acid battery

The world consumption of lead in 1985 was 5.6 Mt and more than 55% of the demand was for the production of lead/acid batteries (starter and traction batteries, stationary installations) [27].

In the charged state the sulphuric acid concentration of the lead/acid battery is about 4.5 moles/litre [82]. Because of the extraordinarily low exchange current density (of the order of 10^{-12} A/cm^2) for the H^+/H_2 reaction the negative pole acts as a reversible lead/lead-sulphate electrode. This electrode is metastable; the lead ought in accordance with Reaction (10) to corrode irreversibly to a mixture of lead sulphide and lead sulphate, which is obviously not the case.

Because of the great economic importance of the lead/acid battery there is an extensive literature in book form (eg [8, 82]) and innumerable individual papers in electrochemical journals are concerned with the investigation of specific aspects. In addition to electrochemical investigation methods, electron-optical and x-ray diffraction (XRD) methods in particular are also used. The factors which limit the life of the batteries have also been investigated intensively (literature in [82]): there are no indications of the formation of lead sulphide.

In the potential-pH diagrams for lead in sulphuric acid in the context of the lead/acid battery, the formation of lead sulphide is always left out of consideration (eg [60]). Nor do the XRD analyses of the solids on the lead electrodes find any indications of the formation of lead sulphide [52, 60]. Stimulated by the results on lead in hot concentrated sulphuric acid (Para 6.2) a specific search was made for lead sulphide on lead electrodes kept in 1 M acid at various potentials [24]. The backs of the lead sulphate layers were once more investigated electron-optically for this purpose. All the findings both at open-circuit voltage and with cathodic polarisation were unequivocally negative.

There is thus no support for the formation of lead sulphide on the negative plate of the accumulator. Presumably such a reaction would have destructive consequences.

8.2 The Weston cell

The Weston cell is used as a secondary voltage standard ([30 and electro-chemical text-books). The cell is represented by the following scheme:

$$+\ Hg/Hg_2SO_4(s)/CdSO_4 \cdot 8/3H_2O(s),\ H_2O/Cd\ \text{amalgam}\ (10\%)\ -$$

The negative pole is the reversible cadmium/cadmium-sulphate electrode.

The Weston cell was developed in 1892 [1] and because of its low temperature-coefficient it quickly displaced other standard cells which had previously been used. Commercially manufactured Weston cells were on request supplied with a calibration certificate from the Physikalish-Technische Reichanstalt [15].

Weston cells are still in use and with careful treatment perform their ask for decades. Vosburgh and Bates [79] measured an average voltage deviation of 0.03 mV for five cells which were still in use after 26 years. This may seem surprising when it is considered that the cadmium sulphate electrode is metastable. Thermodynamically a reduction of sulphate by cadmium would be favoured:

$$SO_4^{2-} + Cd + 2\ H^+ \rightleftarrows 0.25\ CdS + 0.75\ CdSO_4 + H_2O \qquad (11)$$
$$(\Delta G^\circ = -147.85\ kJ:\ \log K = +25.90)$$

The fact that Weston cells can be calibrated and remain stable for decades is an indication of the fact that the corrosion reaction (11) is completely inhibited. The small voltage-drift of the Weston cell is ascribed to changes in the mercury sulphate electrode [30].

9. SULPHUR ACID AND SULPHATE SOLUTIONS AS INERT ELECTROLYTES IN BASIC ELECTROCHEMICAL RESEARCH

In basic electrochemical research sulphuric acid and sulphate solutions are widely used as supporting electrolytes and as such they prove to be redox-inert. Side-reactions of the sulphate would put the reproducibility of electrochemical measurements - for example in connection with the mechanism of iron dissolution [41] - seriously in doubt. Such interfering effects are unknown, however.

Particular weight must be attached to investigations in which electrochemical measurements were combined with characterisation of the sample-surfaces by surface-analysis techniques (eg [37, 53]). Sulphide formation could be detected here with great sensitivity.

In this connection the experiments of Summers and Frese [64] on the reduction of carbon dioxide at ruthenium electrodes must be mentioned. While the carbon dioxide is reduced to methane the sodium sulphate used as the background electrolyte remains unchanged. The authors have used high-sensitivity detection methods to analyse the gas phase (using gas chromatography), the electrode surface (Auger spectroscopy) and the solution (cyclic voltammetry) without finding any reduction products of sulphate.

One of the most investigated reactions in corrosion chemistry is the evolution of hydrogen at metals - especially at iron and steels. Of particular interest in relation to this is the uptake of atomic hydrogen by steel. This process is of great technical and scientific importance as regards embrittlement of the material and hydrogen-induced stress-corrosion. In this connection, in particular, the effect of different substances as embrittlement promoters and inhibitors is being investigated [19, 34, 57].

In these electrochemical investigations sulphuric acid and acidic to alkaline sulphate solutions are among the normal inert electrolytes [36, 46, 49, 50, 56, 58, 84]. Although in such experiments the potential of the metal is below the H^+/H_2 potential nothing is known about sulphate reduction; this also applies to an experimental temperature of 95°C [50].

Kato et al [35] have investigated the hydrogen-permeation behaviour of iron-copper alloys in 0.5 M sulphuric acid with and without hydrogen sulphide and supplemented the electrochemical measurements with surface-analysis investigations. Using photoelectron and Auger spectroscopy, sulphides could only be detected on the surfaces if the samples were in contact with a solution containing hydrogen sulphide. On the samples from solutions without hydrogen sulphide small quantities of sulphur were also found; this, however, was sulphur(VI) and not sulphur(-II). In view of the high detection-sensitivity of these methods and their sensitivity to the oxidation number of an element it is thus possible to rule out sulphide formation in the pure sulphuric acid.

Naturally, when evaluating missing date caution is required. In this case, however, it is necessary to take specifically into account that hydrogen sulphide promotes the uptake of hydrogen by steel even at trace concentrations. Thus a hydrogen sulphide concentration of 0.2 nM increases hydrogen permeation through a steel foil by a factor of 10 [49] (see also [35]). Accordingly one would expect that even a very slight reduction of sulphate at the steel surface would draw attention to itself via permeation rates which increased with time. One would, moreover, have to expect poorly reproducible and scattered individual experiments. This would probably have the result that other supporting electrolytes would be chosen.

10. THE REDOX STABILITY OF OTHER OXOANIONS

The redox stability of the oxoanions clearly follows no simple systematics. While sulphate behaves inertly the analogues chromate can easily be reduced so that redox titrations are possible with chromate. The situation is similar for perchlorate (which can be reduced in aqueous solution only with difficulty) and the analogous permanganate, which because of its easy reducibility is also used in titrimetry.

We shall not enter here into an exhaustive discussion of redox stability. Rather, we shall briefly discuss the behaviour of those oxoanions which occur in the environment and which in principle can participate as oxidising agents in corrosion reactions.

Near surface groundwater in areas used intensively for agriculture can contain nitrate concentrations of the order of 1 mmol/litre. The nitrate in such waters has higher oxidation capacity than the dissolved oxygen (ca 0.25 mmol O_2 per litre) and its involvement in corrosion reactions must therefore be taken into account.

The corrosive effect of sulphur dioxide and hydrogen-sulphite play an important role in polluted atmosphere. For the final-storage situation this corroding agent is irrelevant. Because, however, among other things copper undergoes an interesting corrosion reaction with sulphur dioxide the reducibility of sulphur(IV) will be discussed here.

A further oxoanion which is also present in natural waters is hydrogen carbonate. Like sulphate it is taken to be redox inert. We shall briefly show how the reducibility of hydrogen carbonate would affect the corrosion of metals.

10.1 Corrosion of metals by nitrates

Nitrate is reducible to ammonia in aqueous solutions by base metals such as zinc. In classic qualitative analysis a specific test for nitrate is based on this reaction.

In natural waters (or equivalent model solutions) nitrate has a corrosive effect on unalloyed steel and on zinc when the dissolved oxygen has previously been consumed by a corrosion reaction [38, 39]. Nitrite, nitrogen and ammonium ions were identified as reaction products.

Similar experiments with copper are not known. By analogy with the above-mentioned findings, however, nitrate reduction at copper cannot be ruled out a priori [65, App B]. From the older corrosion literature [5] on learns that copper is attacked even by very dilute nitric acid (0.1-0.5% HNO_3).

In the pH and concentration range of natural waters the following corrosion reactions are thermodynamically possible, for example:

$$NO_3^- + 2\ Cu \rightleftharpoons NO_2^- + Cu_2O \qquad (12)$$
$$(\Delta G^\circ = -74.81\ kJ:\ \log K = +13.11)$$
$$NO_3^- + 8\ Cu + 2\ H^+ + H_2O \rightleftharpoons NH_4^+ + 4\ CU_2O \qquad (13)$$
$$(\Delta G^\circ = -318.81\ kJ:\ \log K = +55.86)$$

It is therefore to be expected that copper, too, is attacked by oxygen-free nitrate-containing water.

10.2 The reduction of sulphur(IV)

Sulphites and sulphur dioxide are commonly used as reducing agents in chemistry. These compounds are, however, redox-amphoteric and can also act oxidatively. In corrosion chemistry the reducibility of sulphur dioxide to sulphide or elementary sulphur is well-known [47, 59]. Copper also is oxidised in moist air in the presence of sulphur dioxide [12]:

$$SO_2(g) + 6\ Cu \rightleftharpoons Cu_2S + Cu_2O \qquad (14)$$
$$(\Delta G^\circ = -78.70\ kJ:\ \log K_p = +13.79)$$

The corrosion products arising in this reaction have been characterised in detail by surface analysis ([12] and the literature cited therein).

10.3 Corrosion by hydrogen carbonate

In dilute aqueous solutions hydrogen carbonate is inert towards reducing agents, although reduction to carbon or methane is thermodynamically possible (Fig 5). The potential-pH diagram of carbon is similar to that of sulphur (Fig 1).

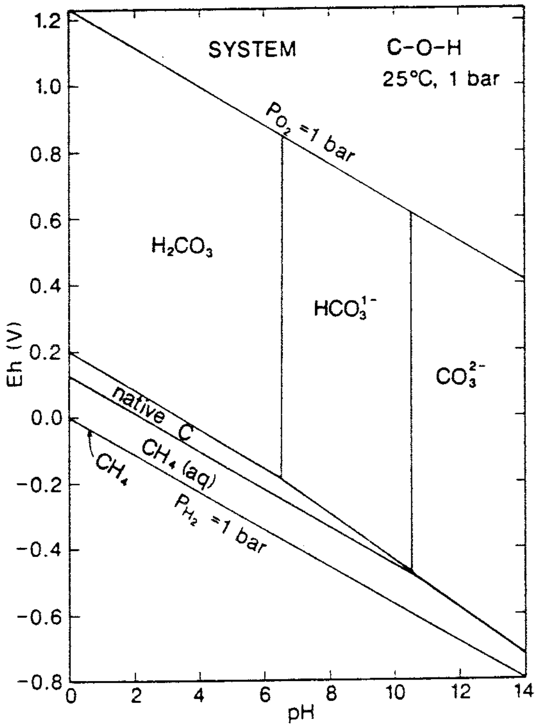

Fig 5.
Potential-pH diagram for the system carbon-water.
$[C]_{tot} = 10^{-3}$ M [9].

There is no lack of experiments on the reduction of carbon(IV) in aqueous solutions. At ruthenium electrodes carbon dioxide can be reduced to methane in hydrogen carbonate solutions at 40-90°C with a low over-voltage and with current efficiencies of 30-40% [64]. The reducible species is carbon dioxide and not hydrogen carbonate. The reduction takes place only at ruthenium and not at other electrode materials (11 metals and semiconductors were investigated).

At other metals, and thus also at copper, carbon dioxide is only reduced at overvoltages of more than one volt with a very low current efficiency [80]. The main product is hydrogen and by mass spectrometry it was possible, using a special experimental set-up, to detect the reaction products methane and ethene. Here, too, the redox-active substance is carbon dioxide and not hydrogen carbonate.

If it is nevertheless assumed that hydrogen carbonate is also reducible then in natural waters the following corrosion reactions, for example, would occur:

$5\ HCO_3^- + 4\ Fe + 5\ H^+ \rightleftarrows CH_4(g) + 4\ FeCO_3 + H_2O$ (15)
($\Delta G^\circ = -495.22$ kJ: $\log K_p = +86.76$)
$HCO_3^- + 3\ Fe + H_2O + H^+ \rightleftarrows CH_4(g) + Fe_3O_4$ (13)
($\Delta G^\circ = -242.21$ kJ: $\log K_p = +42.43$)

The reaction of zinc analogous to Reaction (15) has $\Delta G^\circ = -754.96$ kJ: $\log K_p = +132.3$.

Largescale practical experience over decades exists concerning the corrosion of cast iron and steel and also of galvanised pipes in drinking water supply. In the corrosion literature there are also extremely numerous fundamental investigations of corrosion in natural waters and model solutions. In all the abundance of these experiences there are no indications of the participation of hydrogen carbonate as an oxidising agent.

There is obviously no need to establish in corrosion chemistry a new field of research dealing with the oxidative action of hydrogen carbonate. It is true that hydrocarbons are also formed in the corrosion of carbon steels in acids [31], but they are formed from the carbon in the steel.

11. SUMMARY AND DISCUSSION

The question to be cleared up was whether corrosion of copper by sulphate as the oxidising agent without the involvement of sulphate-reducing bacteria is possible. In order to arrive at firm conclusions it was necessary to extend the scope of the problem to the general question as to whether and under what conditions sulphuric acid and sulphates are chemically or electrochemically reducible.

The evidence presented is multifarious and comes from various fields of chemistry. Apart from a few direct reduction experiments and geochemical findings the main evidence comes from applications of sulphate electrolytes in industrial and scientific electrochemistry and from corrosion reactions.

11.1 The thermodynamics of sulphate corrosion

Thermodynamic considerations show that corrosion reactions of base metals such as iron and zinc by sulphate are in principle possible under the concentration conditions in natural waters. Thermodynamically impossible, however, is the direct reaction of copper and sulphate to give copper(I) sulphide and copper(I) oxide (Reaction (4))[3]. Reaction of copper is only possible if

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[3] Provided the validity of thermodynamics for corrosion reactions is not called in question once more this statement can be regarded as definite (cf Fc, 1).

an additional electron-donor such as iron(II) is available (Reaction (5)).

11.2 Geochemical evidence for the stability of sulphate

In geochemistry, as in inorganic chemistry, it is taken for granted that sulphate is not chemically reducible under the conditions at the earth's surface. Because, however, the involvement of sulphate-reducing bacteria, for example in anaerobic sediments, can never be ruled out with certainty, no decisive importance is attached to the geochemical findings here.

11.3 Experiments on the reduction of sulphuric acid and sulphate

The experiments specifically concerned with the reduction of solutions of sulphuric acid and sulphates ca be divided into three groups.

In the case of <u>hydrothermal experiments</u> on the reduction of zinc sulphate by hydrogen in autoclaves the formation of zinc sulphide can be detected only at 275°C. The oxidation of simple organic compounds such as xylene proceeds only at temperatures above 300°C if the reaction mixture contains hydrogen sulphide as well as sulphate. Without this additive the oxidation of hydrocarbons is even more strongly inhibited. (The role of sulphides in the reduction of sulphate is not discussed in this paper because they oxidise copper directly with the evolution of hydrogen - see Reaction (2)).

The reaction o various <u>metals with sulphuric acid</u> at different concentrations leads to the conclusion that the oxidising effect of the acid starts only at concentrations above 45-50% (6-7 M).

From experiments on the <u>cathodic reduction</u> of sulphuric acid at platinum it is found that the reduction of 12.5 M acid starts, depending on the current density, at 50 to 130°C. There is a further isolated finding that under extreme conditions (110 V cell voltage, point cathode) acids at a concentration around 3 M are still reducible, but not a 0.7 M acid.

Polarographic investigations of sulphuric acid in the concentration range 50-100% lead to the conclusion that the reducible species is not the hydrogen sulphate ion but the undiscussed sulphuric acid molecule.

The first dissociation-constant of sulphuric acid in water is $K_a \sim 10^{+3}$. The concentration of the reducible molecular sulphuric acid is thus very small in dilute acids and negligible in neutral sulphate solutions.

11.4 Corrosion of metals in solutions of sulphuric acid and sulphate

For economic reasons great attention is paid to the corrosion behaviour of metals in the chemical industry and also, for example, in the public watersupply industry. This is not just because of the possible damage to materials but also because of the contamination of chemical products or drinking water by corrosion products.

Copper is resistant to oxygen-free sulphuric acid up to concentrations of 9 M (60%), and also to concentrated solutions of iron sulphate. The thermodynamically possible corrosion reaction (5) thus appears extremely improbable.

Lead is used industrially up to acid concentrations of 13.5 M (78%) as a corrosion-resistant material. At higher concentrations the formation of lead sulphide has been detected experimentally. At an acid concentration of 7 M (50%) this compound was sought but not found. From these experiments too it is thus found that sulphuric acid has an oxidising effect only at a concentration above 7 M.

The industrial production of iron(II) sulphate from iron and hot dilute sulphuric acid can be included among the corrosion processes. Formation of sulphide in accordance with Reaction (3) appears not to occur.

Cast iron and unalloyed and galvanised steel are the normal materials for drinking-water pipes. Although practically all waters also contain sulphate there is no evidence despite decades of technical use of any sulphate reduction. From a taste point of view the drinking water would be impaired as a result of this reaction so that such cases would certainly become known.

It would be possible to add numerous further examples about the corrosion of metals in sulphate solutions and sulphuric acid with the same conclusion.

11.5 Industrial electrochemical processes

Numerous processes industrial electrochemistry are carried out in sulphuric acid or sulphate electrolytes, for example the electrolyte extraction and refining of metals, electroplating and the anodic oxidation of aluminium. The reduction of sulphate would in these processes impair the purity of the products or the optical properties of electrodeposited coatings. Formation of hydrogen sulphide would for health and safety reasons prohibit the carrying out of open processes and necessitate expensive purification of exhaust air. Experience shows that this is not necessary.

Perturbations by reduction products of sulphate would necessitate a switch to sulphate-free variants of the processes (some of which are well-known and also customary) or a switch of production (eg in metal-refining) to non-electrochemical processes.

11.6 Reversible sulphate electrodes

The negative plate of the lead acid cell is the reversible lead/lead-sulphate electrode, despite the fact that thermodynamically the formation of lead sulphide is favoured. Starter batteries have a life of about 5 years and the life of ones in stationary applications is several decades. The formation of lead sulphide at the negative plate would certainly impair the functioning of the accumulator and it would not have been able to achieve success, despite its low energy-density, against other systems. If the negative plate were not stable the Edison cell (nickel-iron alkaline) would probably be used for starter batteries.

The Weston standard cell contains the cadmium/cadmium-sulphate electrode which is unstable relative to cadmium sulphide. The possibility of calibrating these cells and the well-documented high voltage-stability over decades makes it possible to rule out the formation of cadmium sulphide with a high degree of certainty.

11.7 Sulphate solutions as supporting electrolytes

In electrochemical research sulphate solutions and dilute sulphuric acid are used as a matter of course as inert supporting electrolytes. In the clarification of electrochemical reaction mechanisms, especially at cathodic potentials, disturbing factors which would make reproducible precisions-measurements impossible would have to become apparent in an unstable supporting electrolyte. In textbooks and handbooks of electrochemistry the use of such electrolytes would be warned against. This is obviously not the case.

12. CONCLUSIONS

In Sec 2 it was mentioned that strict proof of the redox stability of sulphate in dilute aqueous solution is impossible. From numerous individual pieces of information from various areas of inorganic and industrial chemistry it is, however, possible to define a stability limit with very high certainty. The pieces of evidence presented for the stability of sulphate are of varying quality and evidential value. Particular weight must be placed on those applications where sulphate-reduction puts the precision of measurements in question (Weston cell, basic electrochemical research). The fault-free operation of the negative plate of the lead/acid battery is demonstrated less by precision measurements than by the fact that it carries out its task every day in ca 450 million vehicles [27].

The arguments derived from industrial electrochemistry are stronger the higher are the purity standards required to the product: the tonnage is only a secondary assessment criterion. Possible health-and-safety consequences of the reduction of sulphate in large-scale processes can be included in the arguments.

The final assessment leads to confirmation of the poorly documented chemical teaching (Sec 1) that sulphuric acid and sulphate solutions are not oxidising agents. The probability that the reduction of sulphate has been overlooked in the wide use of sulphate electrolytes in science and technology must be regarded as extremely small.

With a large margin of safety the limit of the redox stability of sulphuric acid can be set at a concentration of ca 4 M (acid concentration in the lead/acid battery). Slightly acidic to alkaline sulphate solutions, on the other hand, are completely redox-inert in concentration and temperature ranges which can be achieved in open vessels in the laboratory.

It is nevertheless difficult to give a numerical limit for the reaction rate of sulphate reduction because there are no systematic kinetic measurements at high at high temperatures and so the activation energies needed for extrapolation are not known. From the work of Kato et al [35] (cf Sec 9] it is nevertheless possible to derive a limit for the current efficiency for sulphuric acid reduction.

These authors developed hydrogen for 24 hours at iron-copper alloys using a current density of 5 mA/cm^2. The surfaces of the samples were then analysed using photoelectron and Auger spectroscopy and no sulphide sulphur was detected. Photoelectron spectroscopy provides evidence of the oxidation number of the elements present. The detection limit of this method is 0.1 ng/cm^2, which corresponds to around 1% of a monolayer [13]. The detection sensitivity of Auger spectroscopy is 1-3 orders of magnitude better.

The results were as follows. During the experiment at total charge of 432 coulombs/cm^2 (4.5 x 10^{-3} faradays) flowed and 2.25 x 10^{-3} mols of hydrogen were produced. During the same period less than 0.1 ng (3.1 x 10^{-12} mol) of sulphide per cm^2 was deposited. To reduce the corresponding amount of sulphate 2.5 x 10^{-11} faradays would have been required. It is thus possible to calculate for sulphate reduction a limit for the faraday efficiency (current efficiency):

$$\eta_F \leq 5.6 \cdot 10^{-9}$$

The molar yield ($S(-II)/H_2$) is

$$\eta_{mol} \leq 1.4 \cdot 10^{-9}$$

These values apply to an acidic solution and strong cathodic polarisation: they are thus in no way representative of a corrosion reaction at a low sulphate concentration in neutral solution and considerably higher electrode potentials. For these milder reaction conditions the limits stated above can be regarded as extremely conservative.

If we arbitrarily assume a sulphate reduction of 3 x 10^{-12} mol/cm^2/day then purely mathematically one obtains for the corrosion of copper to Cu_2S an induced material loss of 0.15 nm/year or 150 µm in 10^6 years.

Thus corrosion of copper by sulphate under final-storage conditions in the absence of sulphide reducing bacteria can be ruled out with a probability verging on certainty especially because the reaction would also require an additional electron-donor. Also, from the wide field of corrosion chemistry no case is known where sulphate in dilute solution acts as an oxidising agent. Any contrary finding would be the chemical equivalent of discovering a new continent (see Fn.2).

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List of SKB reports

Annual Reports

1977-78
TR 121
KBS Technical Reports 1 – 120
Summaries
Stockholm, May 1979

1979
TR 79-28
The KBS Annual Report 1979
KBS Technical Reports 79-01 – 79-27
Summaries
Stockholm, March 1980

1980
TR 80-26
The KBS Annual Report 1980
KBS Technical Reports 80-01 – 80-25
Summaries
Stockholm, March 1981

1981
TR 81-17
The KBS Annual Report 1981
KBS Technical Reports 81-01 – 81-16
Summaries
Stockholm, April 1982

1982
TR 82-28
The KBS Annual Report 1982
KBS Technical Reports 82-01 – 82-27
Summaries
Stockholm, July 1983

1983
TR 83-77
The KBS Annual Report 1983
KBS Technical Reports 83-01 – 83-76
Summaries
Stockholm, June 1984

1984
TR 85-01
Annual Research and Development Report 1984
Including Summaries of Technical Reports Issued during 1984. (Technical Reports 84-01 – 84-19)
Stockholm, June 1985

1985
TR 85-20
Annual Research and Development Report 1985
Including Summaries of Technical Reports Issued during 1985. (Technical Reports 85-01 – 85-19)
Stockholm, May 1986

1986
TR 86-31
SKB Annual Report 1986
Including Summaries of Technical Reports Issued during 1986
Stockholm, May 1987

1987
TR 87-33
SKB Annual Report 1987
Including Summaries of Technical Reports Issued during 1987
Stockholm, May 1988

1988
TR 88-32
SKB Annual Report 1988
Including Summaries of Technical Reports Issued during 1988
Stockholm, May 1989

1989
TR 89-40
SKB Annual Report 1989
Including Summaries of Technical Reports Issued during 1989
Stockholm, May 1990

Technical Reports

List of SKB Technical Reports 1991

TR 91-01
Description of geological data in SKB's database GEOTAB
Version 2
Stefan Sehlstedt, Tomas Stark
SGAB, Luleå
January 1991

TR 91-02
Description of geophysical data in SKB database GEOTAB
Version 2
Stefan Sehlstedt
SGAB, Luleå
January 1991

TR 91-03
1. The application of PIE techniques to the study of the corrosion of spent oxide fuel in deep-rock ground waters
2. Spent fuel degradation
R S Forsyth
Studsvik Nuclear
January 1991

TR 91-04
Plutonium solubilities
I Puigdomènech[1], J Bruno[2]
[1]Enviromental Services, Studsvik Nuclear, Nyköping, Sweden
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February 1991

TR 91-05
Description of tracer data in the SKB database GEOTAB
SGAB, Luleå
April, 1991

TR 91-06
Description of background data in the SKB database GEOTAB
Version 2
Ebbe Eriksson, Stefan Sehlstedt
SGAB, Luleå
March 1991

TR 91-07
Description of hydrogeological data in the SKB's database GEOTAB
Version 2
Margareta Gerlach[1], Bengt Gentzschein[2]
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[2]SGAB, Uppsala
April 1991

TR 91-08
Overview of geologic and geohydrologic conditions at the Finnsjön site and its surroundings
Kaj Ahlbom[1], Sven Tirén[2]
[1]Conterra AB
[2]Sveriges Geologiska AB
January 1991

TR 91-09
Long term sampling and measuring program. Joint report for 1987, 1988 and 1989. Within the project: Fallout studies in the Gideå and Finnsjö areas after the Chernobyl accident in 1986
Thomas Ittner
SGAB, Uppsala
December 1990

TR 91-10
Sealing of rock joints by induced calcite precipitation. A case study from Bergeforsen hydro power plant
Eva Hakami[1], Anders Ekstav[2], Ulf Qvarfort[2]
[1]Vattenfall HydroPower AB
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January 1991

TR 91-11
Impact from the disturbed zone on nuclide migration – a radioactive waste repository study
Akke Bengtsson[1], Bertil Grundfelt[1],
Anders Markström[1], Anders Rasmuson[2]
[1]KEMAKTA Konsult AB
[2]Chalmers Institute of Technology
January 1991

TR 91-12
Numerical groundwater flow calculations at the Finnsjön site
Björn Lindbom, Anders Boghammar,
Hans Lindberg, Jan Bjelkås
KEMAKTA Consultants Co, Stockholm
February 1991

TR 91-13
Discrete fracture modelling of the Finnsjön rock mass
Phase 1 feasibility study
J E Geier, C-L Axelsson
Golder Geosystem AB, Uppsala
March 1991

TR 91-14
Channel widths
Kai Palmqvist, Marianne Lindström
BERGAB-Berggeologiska Undersökningar AB
February 1991

TR 91-15
Uraninite alteration in an oxidizing environment and its relevance to the disposal of spent nuclear fuel
Robert Finch, Rodney Ewing
Department of Geology, University of New Mexico
December 1990

TR 91-16
Porosity, sorption and diffusivity data compiled for the SKB 91 study
Fredrik Brandberg, Kristina Skagius
Kemakta Consultants Co, Stockholm
April 1991

TR 91-17
Seismically deformed sediments in the Lansjärv area, Northern Sweden
Robert Lagerbäck
May 1991

TR 91-18
Numerical inversion of Laplace transforms using integration and convergence acceleration
Sven-Åke Gustafson
Rogaland University, Stavanger, Norway
May 1991

TR 91-19
NEAR21 - A near field radionuclide migration code for use with the PROPER package
Sven Norman[1], Nils Kjellbert[2]
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April 1991

TR 91-20
Äspö Hard Rock Laboratory. Overview of the investigations 1986-1990
R Stanfors, M Erlström, I Markström
June 1991

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Äspö Hard Rock Laboratory. Field investigation methodology and instruments used in the pre-investigation phase, 1986-1990
K-E Almén, O Zellman
June 1991

TR 91-22
Äspö Hard Rock Laboratory. Evaluation and conceptual modelling based on the pre-investigations 1986-1990
P Wikberg, G Gustafson, I Rhén, R Stanfors
June 1991

TR 91-23
Äspö Hard Rock Laboratory. Predictions prior to excavation and the process of their validation
Gunnar Gustafson, Magnus Liedholm, Ingvar Rhén, Roy Stanfors, Peter Wikberg
June 1991

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Hydrogeological conditions in the Finnsjön area. Compilation of data and conceptual model
Jan-Erik Andersson, Rune Nordqvist, Göran Nyberg, John Smellie, Sven Tirén
February 1991

TR 91-25
The role of the disturbed rock zone in radioactive waste repository safety and performance assessment. A topical discussion and international overview.
Anders Winberg
June 1991

TR 91-26
Testing of parameter averaging techniques for far-field migration calculations using FARF31 with varying velocity.
Akke Bengtsson[1], Anders Boghammar[1], Bertil Grundfelt[1], Anders Rasmuson[2]
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[2]Chalmers Institute of Technology

TR 91-27
Verification of HYDRASTAR. A code for stochastic continuum simulation of groundwater flow
Sven Norman
Starprog AB
July 1991

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Radionuclide content in surface and groundwater transformed into breakthrough curves. A Chernobyl fallout study in an forested area in Northern Sweden
Thomas Ittner, Erik Gustafsson, Rune Nordqvist
SGAB, Uppsala
June 1991

TR 91-29
Soil map, area and volume calculations in Orrmyrberget catchment basin at Gideå, Northern Sweden
Thomas Ittner, P-T Tammela, Erik Gustafsson
SGAB, Uppsala
June 1991

TR 91-30
A resistance network model for radionuclide transport into the near field surrounding a repository for nuclear waste (SKB, Near Field Model 91)
Lennart Nilsson, Luis Moreno, Ivars Neretnieks, Leonardo Romero
Department of Chemical Engineering, Royal Institute of Technology, Stockholm
June 1991

TR 91-31

Near field studies within the SKB 91 project

Hans Widén, Akke Bengtsson, Bertil Grundfelt
Kemakta Consultants AB, Stockholm
June 1991

TR 91-32

SKB/TVO Ice age scenario

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[2]Teollisuuden Voima Oy (TVO)
[3]Svensk Kärnbränslehantering AB (SKB)
June 1991

TR 91-33

Transient nuclide release through the bentonite barrier - SKB 91

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May 1991

TR 91-34

SIMFUEL dissolution studies in granitic groundwater

I Casas[1], A Sandino[2], M S Caceci[1], J Bruno[1], K Ollila[3]
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TR 91-35

Storage of nuclear waste in long boreholes

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[1]Tyréns
[2]Clay Technology AB
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August 1991

TR 91-36

Tentative outline and siting of a repository for spent nuclear fuel at the Finnsjön site. SKB 91 reference concept

Lars Ageskog, Kjell Sjödin
VBB VIAK
September 1991

TR 91-37

Creep of OFHC and silver copper at simulated final repository canister-service conditions

Pertti Auerkari, Heikki Leinonen, Stefan Sandlin
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September 1991

TR 91-38

Production methods and costs of oxygen free copper canisters for nuclear waste disposal

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Outokumpu Poricopper Oy, Finland
June 1991