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RADIOLYTIC CORROSION AND RELATED PROBLEMS IN THE COOLING
WATER CIRCUITS OF HIGH-ENERGY PARTICLE ACCELERATORS

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SUMMARY

Copper(II) ion production by radiolytic effects in the RF-cooling water circuit of the CERN 600 MeV Synchro-cyclotron was determined. Corrosion inhibitors, such as hydrazine and benzotriazole, were added to the water in a "circuit-simulator" and the corrosion rate under irradiation conditions was studied. Later, these inhibitors were directly applied to the water of the RF-cooling circuit and their behaviour was examined.

Beam intensity, water flow rate, available copper surface and temperature were kept constant and the dependence of copper(II) ion production on irradiation time was determined. Through this experiment it was possible to derive a law $C \sim \sqrt{t}$ for the time (t) dependence of the increase of copper(II) ion concentration (C). It could be shown too, that corrosion of copper surfaces in an irradiated water circuit follows a law which is different from that for "normal" corrosion in pure demineralized (but oxygen-containing) water.

Benzotriazole, as an inhibitor, behaved as if the available copper surface had been reduced. For hydrazine, the inhibitive effect was disturbed by the quick copper catalyzed decomposition of this compound.

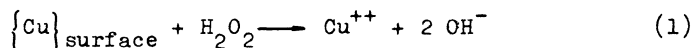
1. INTRODUCTION

Corrosion of the copper surfaces in cooling water tubes which are irradiated in a few places by high-energy particles and their secondaries, is mainly due to oxidation by radiolytic decomposition products of water. Among the decomposition products of irradiated water formed, $\cdot\text{OH}$ -radicals, their combination H_2O_2 , H_2O^\cdot -radicals and H_2^+ -ions are responsible for the corrosion of copper surfaces. (Van de Voorde has recently presented a collection of literature on radiolytic effects in water^{1,2,3}.)

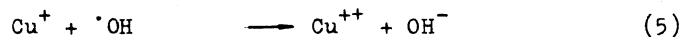
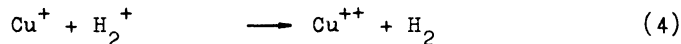
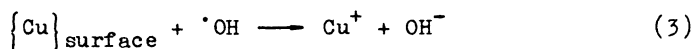
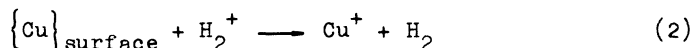
The present work was undertaken in order to find the analytical rate of copper(II) ion production by radiolytic corrosion and to propose a method for either avoiding corrosion or extending the intervals between water purification processes by ion exchange.

2. GENERAL ASPECTS

In a simplified manner the decisive corrosive reactions can be written as follows:



and,



In other words, the concentration of copper(II) ions in a solution will increase as well as the pH value (OH^- production). As reactions (1), (4) and (5) show, mainly Cu(II) will be formed.

In addition, some hydrogen and oxygen gas is formed [the latter, for example, by the reaction $2 \text{HO}^\cdot \longrightarrow \text{H}_2\text{O}_2 + \text{O}_2$ ²] and by decomposition of hydrogen peroxide]. As a result of these processes the water will soon be saturated with oxygen (approximately 8 mg O_2 /l). Then the increase of the hydrogen peroxide net concentration is a linear function of the absorbed dose⁴).

Fortunately, the production of some OH^- which increases the pH values slows down the reaction between copper and hydrogen peroxide as well as the radiation-induced production of hydrogen peroxide. The copper ion catalyzed decomposition of hydrogen peroxide might have a similar influence on the formation of additional copper(II) ions.

The increasing copper(II) concentration in the closed cooling water circuit causes some troubles: because the conductivity of water increases proportionally to the ion concentration, the isolating properties decrease. Deposits of corrosion products may also be formed and sedimented in certain parts of the circuit. (Deposits of black CuO have already been found near some tube connections.)

To avoid these problems, the water has to be regenerated at regular intervals by means of mixed bead ion exchange columns, a process which consumes much time and manpower (approximately 24 h per run). At present regeneration has to be carried out whenever the conductivity of the cooling water reaches a value of $15 \mu \Omega^{-1} \text{cm}^{-1}$, which happens practically every three days for the Synchro-cyclotron RF-cooling water circuit.

3. CORROSION INHIBITORS

Corrosion of copper tubes in cooling water circuits is a common and well known problem in industry. Numerous reagents have been applied depending on the working conditions of the circuit.

A very simple method would consist in fixing the pH-value of the water at 8-9. Owing to the need of maintaining low conductivity this solution is not applicable in the case under consideration. There also exists the possibility of working with large gas spaces or in open circuits so that the hydrogen peroxide production equilibrium is disturbed by the escape of the gases formed. This method is usually very inconvenient and often not practicable. The same argument applies if a large amount of hydrogen gas is added which would slow down the production of hydrogen peroxide during irradiation. A radical (although expensive) method would be to exchange the copper tubes to aluminium ones.

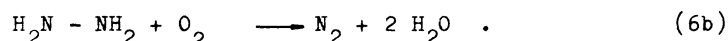
However, these problems with copper tubes can be solved by adding to the water chemical surface protecting or inhibitive products. There are two ways of influencing the reaction:

- a) addition of a strongly reducing reagent which reacts more quickly with the active oxygen formed than with the copper surface, and
- b) addition of a reagent which forms an insoluble compound with copper ions and protects the surface against oxygen by means of a resistant surface layer.

Since there are two ways of influencing the reaction two groups of chemical products can act as corrosion inhibitors:

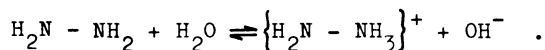
3.1 Hydrazine

We take hydrazine ($\text{H}_2\text{N}-\text{NH}_2$) as representative for reducing reagents especially because of the simplicity of the reaction products formed⁵⁾. It reacts with hydrogen peroxide or oxygen in forming water and nitrogen:



Furthermore, it is easy to control its concentration in water by means of an oxydometric titration with standard I_2 -solution.

Reaction (6b) has a fast reaction velocity in the presence of a catalyser, for example Cu(II). This means that the reaction is practically self-catalyzing after the first traces of copper ions have been formed. Hydrazine solutions are slightly alkaline which is another advantage for the copper system:

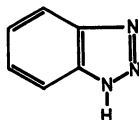


But formation of ions means increase of conductivity and consequently for the present problem the concentration of hydrazine must not be too high. Another disadvantage in using hydrazine is its weak stability and especially in the presence of a catalyser like Cu(II), its decomposition. To maintain the protective properties of the concentration -- which has to offer a compromise between the required conductivity and inhibitive effectiveness -- a certain amount of hydrazine should be added to the solution at regular intervals.

3.2 Benzotriazole

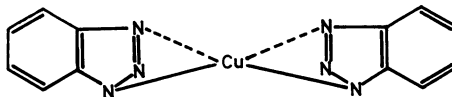
For chemical reactions forming insoluble copper precipitates and surface layers, a group of organic compounds, such as indole, indazole, benzimidazole, benzotriazole and their derivatives have recently been examined and applied^{6,7}). Of these compounds the most promising seemed to be benzotriazole.

BENZOTRIAZOLE

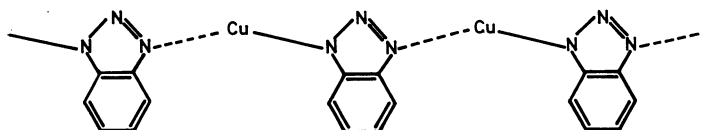


It reacts with both Cu(I) and Cu(II) to form insoluble precipitates and its tarnish resistance is considered good. It forms copper complexes of the following compositions:

Cu(II)



Cu(I)



But the radiation resistance of benzotriazole has not yet been examined. Because of its resonance structure the compound should be quite stable, but will certainly be damaged after a period of irradiation. This means that benzotriazole in small concentrations should be added regularly to the water to replace the decomposed part.

4. EXPERIMENTAL TECHNIQUES

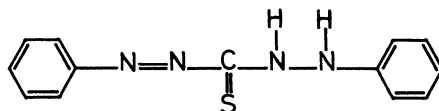
To solve the specific problem of radiation-induced corrosion of copper tubes a microanalytical method had to be applied for the copper determination. Moreover, to get an idea of the effects involved, a "simulator" was constructed to work in a small circuit at high radiation doses without disturbing the routine work of the machine. All inhibitors were first examined in this simulator and later applied to the circuit. Measurements of the increase of copper ion concentration could be made at short

time intervals for experiments with the simulator, while water samples from the real circuit were taken only once a day.

4.1 Microanalytical copper determination

One of the most sensitive microanalytical methods for copper determination is the liquid-liquid extraction of the copper dithizone complex followed by a colorimetric measurement of the colour change^{8,9}).

DITHIZONE (short form) = DIPHENYLTHIOCARBAZONE



A dithizone solution in tetrachlorocarbon or chloroform has a dark green colour, the Cu(II) complex of the reagent in the same solvent is red. As long as there is a surplus of dithizone in the solution the colour will be green-blue to grey-blue, depending on the copper concentration. If one reaches a total colour change from green to red during extraction the procedure has to be repeated with smaller copper concentrations because the Lambert-Beer law is no longer valid. The method is very sensitive for copper concentrations in the range 0.01 - 0.5 ppm, if other metals, especially Ag, Au, Be, Fe(III), Hg, Pd, Tl(III), are absent, as is in practice the case in the present problem.

4.1.1 Cu(II) extraction with dithizone

Reagents : 0.002% w/v solution of dithizone in CCl₄ (freshly prepared every day from a more stable stock solution 0.01% w/v),
HCl, concentrated;

Procedure : 10 ml of water sample containing not more than 5 µg Cu(II) are pipetted into a Squibb type separatory funnel holding 100 ml.

Two drops of concentrated HCl are added so that the pH reaches a value between 1 and 2;

Five ml of standard dithizone solution are added and the funnel agitated vigorously for two minutes (this time interval must be kept constant for all extractions because of the colour fading of the dithizone solution);

After separation of the aqueous and organic layer (approximately one minute) and elimination of eventual water drops in the funnel exit, the organic phase is transferred to a 1 cm colorimetric cell and measured in a colorimeter.

4.1.2 Colorimetric measurement

The transmittance of the samples containing copper was measured at a wavelength of 535 mµ in a ZEISS PMQ II Photometer. The pure standard reagent was taken as reference by setting its transmittance to 100%.

A calibration plot was made with known Cu(II) solutions containing 0.5, 1, 2, 3, 4 and 5 $\mu\text{g Cu}^{++}$ per 10 ml ultrapure water.

Two to three independent copper determinations were made from each of the water samples taken in the experiments. The measured transmittance was compared with the calibration plot. The relative errors of this method were in the region of 2%, the pipetting error being of the order of 0.1-0.2% when working with absolutely calibrated pipettes. Thus, the overall error should not exceed 2.5%. The results are given in mg Cu^{++}/l water (ppm).

4.2 The "circuit-simulator"

A copper chamber was constructed to obtain greater copper(II) ion production rates at short time intervals and was exposed to the external 600 MeV proton beam of the Synchro-cyclotron. The beam intensities are given in the tables. The simulator may also be used to examine eventual corrosion inhibitive products. This chamber is shown in fig. 1. It contains 19 removable 10x10 cm copper plates placed at 1 cm from each other. Because the inside of the lid is covered with rubber, the total surface available amounts to 4,600 cm^2 .

A pump keeps the water circulating at a constant flow rate through the chamber. The total volume of the chamber, pump and hoses is 2.15 l. Samples can be taken by means of a cock in the plastic hose. The volume of water taken is continuously re-filled, simply by keeping the funnel on top of the chamber full of water. The conductivity and temperature are measured directly in the circuit. The position of the proton beam passing through the chamber is observed by means of a scintillating screen.

4.3 Experiments in the simulator and in the RF-cooling water circuit

After the first determinations of increasing copper ion concentration in the RF-cooling water circuit, a simulator was constructed in which all further experiments were first performed and the methods found were then applied to the real circuit. Figure 2 shows the present state of the RF-cooling water circuit with the irradiation areas indicated (X).

4.3.1 Radiolytic corrosion by demineralized water

4.3.1.1 Increase of the Cu(II) concentration in water circulating through the simulator without irradiation

To find the difference between radiation-induced corrosion of copper surfaces and "normal" corrosion, an experiment was carried out with water pumped through the simulator without irradiation. Samples were taken at the same time intervals as during irradiation experiments. The conductivity was measured in the circuit and the results are given in table 1. Figure 3 gives the results of all the experiments, curve 1 represents the data given below.

Table 1

time (hours)	$\frac{\text{mg Cu}^{++}}{\text{l}}$	conductivity ^{*)} $\mu\Omega^{-1}\text{cm}^{-1}$	pH
0	0.018	2.5	5.90
1/6	0.42	3.0	6.42
1/2	0.60	3.8	6.43
1	0.68	4.1	6.46
2	0.80	4.5	6.52
5	0.98	5.5	6.62
10	1.21	6.2	6.74

*) All conductivity values given are measured by an AC instrument.

4.3.1.2 Irradiation of water circulating through the simulator

After cleaning, the simulator was refilled with demineralized water and exposed to the proton beam which entered through the middle of the front-plate. At given time intervals the beam was interrupted, a sample taken and the instruments read. The simulator was therefore working for more than 10 hours (11 h, 9 min), but this fact was not taken into consideration because copper corrosion is much more apparent in this case than without irradiation. Table 2 shows the results. (See also fig. 3, curve 2.)

Table 2

time (hours)	$\frac{\text{mg Cu}^{++}}{\text{l}}$	conductivity $\mu\Omega^{-1}\text{cm}^{-1}$	pH	average proton flux
0	not measured	5.0	5.90	$2.4 \cdot 10^{11}$ p/cm ² sec
1/6	1.28	6.0	6.32	
1/2	2.62	9.0	6.46	
1	3.80	13.5	6.59	
2	5.60	19.0	6.66	
5	8.30	29.5	6.90	
10	11.24	38.5	6.86	

4.3.1.3 Increase of the Cu(II) concentration in the RF-circuit

The Cu(II) production is naturally much slower in the circuit than in the simulator, particularly because only small areas are irradiated. Nevertheless, the conductivity of this water increases quickly in parallel with copper ion concentration. Table 3 shows one of the typical measurements made in the circuit during machine operation.

Table 3

time *) (hours)	mg Cu ⁺⁺ l	conductivity $\mu\Omega^{-1} \text{ cm}^{-1}$	pH
1	0.63	3.5	6.10
18	0.9	5.5	-
30	1.7	12	-
42	1.9	13	6.78

*) Time taken from end of regeneration.

4.3.2 Corrosion after addition of hydrazine

4.3.2.1 Increase of the Cu(II) concentration without irradiation

The first additions of hydrazine [1 mmole = 50 mg $(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$ per litre] made the conductivity too high, whereas an oxidimetric titration of hydrazine showed that about 14 mg/l of hydrazine had already disappeared after one hour's run in the simulator. This amount is equivalent to 9 mg of oxygen per litre which is approximately the value of a saturation concentration. This fact was taken into consideration for the experiment: the hydrazine concentration was measured before the start and hydrazine was added up to a concentration of approximately 0.5 mmole/l. Table 4 shows the results of this run. (See also fig. 3, curve 3.)

Table 4

time (hours)	mg Cu ⁺⁺ l	conductivity $\mu\Omega^{-1} \text{ cm}^{-1}$	pH	initial hydrazine concentration
0	0.11	8.5	6.45	28.0 mg/l $(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$
1/6	0.33	8.5	6.55	
1/2	0.42	8.5	6.60	
1	0.48	8.1	6.63	
2	0.63	8.1	6.60	
5	0.90	8.5	6.60	
10	1.02	8.8	6.61	

The typical differences with respect to the results given in table 1 are apparent: pH and conductivity remain practically constant even though the copper corrosion is not much less than before.

This can be explained by the decomposition of hydrazine during formation of copper ions and by reaction with oxygen (conductivity) as well as by a buffer effect of the weakly alkaline reagent (pH value). It is worth noting that the absolute value of conductivity is larger than before, and practically all the hydrazine is used up in the experiment.

4.3.2.2 Irradiation of hydrazine-containing water in the simulator

The simulator was cleaned, refilled with water containing 28.5 mg hydrazine hydrate per liter and irradiated. Table 5 shows the results. (See also fig. 3, curve 4.)

Compared to the results given in paragraph 4.3.1.2 (table 2), copper (II) ion production is slower and at maximum exposure time reaches about 78% of the value found in pure water. pH values stay practically constant and conductivity increases much more slowly than for pure irradiated water. The hydrazine had totally disappeared at the end of the exposure.

Table 5

time (hours)	$\frac{\text{mg Cu}^{++}}{\text{l}}$	conductivity $\mu\Omega^{-1} \text{ cm}^{-1}$	pH	average proton flux	initial hydrazine concentration
0	0.14	12	6.48	$2.7 \cdot 10^{11}$ p/cm ² sec	28.5 mg/l (NH ₂) ₂ · H ₂ O
1/6	0.37	12	6.48		
1/2	1.48	12	6.38		
1	2.40	14	6.44		
2	3.64	18	6.48		
5	6.05	22	6.58		
10	8.80	24	6.64		

4.3.2.3 Cu(II) increase in the RF-circuit

In the first run 63.7 g of hydrazine hydrate were added to the water of the RF circuit. This is equivalent to 35 mg of hydrazine hydrate per litre for the 1500 l total contents. Analysis of the water samples showed that the hydrazine had disappeared after one day and therefore another 30 g of hydrazine were added. The conductivity increased after the addition of hydrazine but stayed constant much longer than normally. Table 6 gives the results of this first run. The experiment was repeated soon after, but hydrazine hydrate only once was added (58.2 g) to the water. Table 7 shows the data for this second run.

Table 6

time (hours)	$\frac{\text{mg Cu}^{++}}{\text{l}}$	conductivity $\mu\Omega^{-1} \text{ cm}^{-1}$	pH
0 [*])	1.10	11	6.60
1 $\frac{1}{2}$	1.15	10	6.36
19	1.45	11.5	6.42
19	Further addition of $(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$. Conductivity increases to $14.5 \mu\Omega^{-1} \text{ cm}^{-1}$.		
25 $\frac{1}{2}$	1.95	13	6.44
42 $\frac{1}{2}$	2.05	13	6.47
49 $\frac{1}{2}$	2.05	13	6.52
114 $\frac{1}{2}$	2.22	15	6.58

*) After regeneration, directly before adding 63.7 g of hydrazine.

Table 7

time (hours)	$\frac{\text{mg Cu}^{++}}{\text{l}}$	conductivity $\mu\Omega^{-1} \text{ cm}^{-1}$
0 [*])	0.582	3.8
3 $\frac{1}{2}$	1.404	6.8
23	1.875	8.5
47 $\frac{1}{2}$	1.910	9.5
70 $\frac{1}{2}$	2.020	11
142	2.135	13.5

*) After regeneration, directly before adding 58.2 g of hydrazine.

A subsequent control run without adding hydrazine gave a surprising result: there was less copper(II) ion production than in the case reported in table 7. A certain surface protection layer must have been formed by the hydrazine which had been circulating before. Table 8 shows these determinations. After the next regeneration cycle, however, the values of table 3 could once again be reproduced. Therefore, hydrazine gave only a preliminary surface protection during and directly after a run.

This might also explain the slightly better results of the second run compared to the first one.

Table 8

time (hours)	$\frac{\text{mg Cu}^{++}}{\text{l}}$	conductivity $\mu\Omega^{-1} \text{ cm}^{-1}$
0 ^{*)}	0.554	3
25	1.025	7
47 $\frac{1}{2}$	1.415	9.5
70 $\frac{1}{2}$	1.815	11
144	1.870	14

*) End of regeneration cycle.

4.3.3 Corrosion after addition of benzotriazole

For the examination of the inhibitive properties of benzotriazole, the producer (GEIGY in Basle) kindly sent us a free sample of the reagent. Because of the limited quantity of this sample the reagent was at once used for an irradiation experiment in the simulator, the run without irradiation being omitted.

4.3.3.1 Irradiation of water in the benzotriazole-treated simulator

Benzotriazole can be used in two ways:

- i) circulation of water containing 0.1 - 0.5% w/v of reagent and occasional addition of fresh product to replace that used,
- ii) preparation of the copper surfaces with a hot benzotriazole solution to build a protective layer.

To test the product under what were considered the worst conditions, i.e. no replacement of used or damaged surface layer, the second method was chosen.

The simulator was filled with a 0.5% w/v solution of benzotriazole (pH:5.65) heated to 60°C. After half an hour the solution was removed, filtered, and after cooling down returned to the simulator which had been thoroughly washed with distilled water. The solution was left in the chamber for 2 $\frac{1}{2}$ days, then poured out and the simulator was well rinsed with bi-distilled water.

Afterwards the simulator was filled with bi-distilled water, but had to be left for another 22 hours before the experiment could be started. The results are given in table 9. (See also fig. 3, curve 5.)

Table 9

time (hours)	$\frac{\text{mg Cu}^{++}}{\text{l}}$	conductivity $\mu\Omega^{-1} \text{ cm}^{-1}$	average proton flux
1/6	0.86	6	$2.35 \cdot 10^{11}$ p/cm ² sec
1/2	1.33	8	
1	2.09	11	
2	2.95	12 - 15 ^{*)}	
5	4.20	16	
10	6.10	22 - 26 ^{*)}	

*) Measured at beginning and end of time interval.

Even though the conditions were worse (22 h in simulator before start of experiment, 70 min interruption after two hours of irradiation because of a machine stop), the copper concentration was only 54% of that reached when pure water was irradiated in the simulator (table 2).

4.3.3.2 Application of benzotriazole in the RF-circuit

Three kilograms of benzotriazole were added to the water of the RF-circuit (0.2% w/v solution). Because of the low solubility of benzotriazole the product could not be added in dissolved form but as a solid compound. Three bags (nylon stockings), each filled with 1 kg of benzotriazole were immersed in two of the tanks of the circuit (2a and 2b in fig. 2). About 24 hours later the product was completely dissolved and the bags could be taken out. The water had been demineralized before the product was added and showed a pH value of 6.05 and a conductivity of $4 \mu\Omega^{-1} \text{ cm}^{-1}$.

The conductivity increased to $12 \mu\Omega^{-1} \text{ cm}^{-1}$ while the product was dissolving whereas the pH decreased to a value of 5.5. The copper(II) ion concentration was measured every 24 hours except at week-ends and during routine maintenance periods. Table 10 gives the results of these measurements. The initial copper(II) concentration decreased rapidly from 0.8 ppm to below 0.1 ppm and remained constant during the period of observation (approximately three weeks). It was necessary neither to regenerate the water nor to add more benzotriazole during this period.

After three weeks the water was regenerated and then showed a conductivity of $2.8 \mu\Omega^{-1} \text{ cm}^{-1}$. The next run of RF-cooling was considered as a "control run" as in the case of hydrazine (Chapter 4, paragr. 4.3.2.3) and no benzotriazole was added. This control proved that benzotriazole had indeed produced a resistive tarnish layer because the conductivity of the water increased only very slowly to a value of $12 \mu\Omega^{-1} \text{ cm}^{-1}$ after 32 days of cycling through the circuit.

Table 10

time (hours)	$\frac{\text{mg Cu}^{++}}{\text{l}}$	conductivity $\mu\Omega^{-1} \text{ cm}^{-1}$	pH
0	0.85	4.5	6.05
24	0.16	12	5.6
48	0.14	13.5	5.6
120	0.1	14	5.5
144	0.1	14.5	5.6
189 $\frac{1}{2}$	0.1	~ 15	5.7
192	0.13	~ 15	5.7
216	0.1	13.5	5.6
287	<0.1	14	5.6
312	<0.1	14	5.6
360	<0.1	14	5.7
384	<0.1	14	5.6
456	<0.1	16	5.8

Note: Maintenance after 165 and 333 hours.

5. DISCUSSION

Obviously, benzotriazole gave by far the best results among the inhibitors examined. For a better discussion and comparison of the results found in the simulator experiments, the time dependence of the corrosive effect was drawn in a double logarithmic scale. Then the curves of fig. 3 became straight lines, and these lines showed the same slope for pure irradiated water and for benzotriazole containing water (see fig. 4).

Mathematically, the equation for a straight line in double logarithmic scale can be expressed by

$$\log C \sim K \log t \quad (8)$$

or,

$$C = A t^k \quad (8a)$$

where, C : concentration of Cu^{++} in solution,
t : time in hours,
A, k : constants.

A statistical averaging method for the data found (see tables 1, 2, 5, 9) was applied to calculate the parameters of Eq. 8a. For the range $t = 1/6$ h to $t = 10$ h this gave:

(a) pure water	$C = 3.75 t^{0.495} \approx 3.75 \sqrt{t}$
(b) hydrazine added	$C = 2.35 t^{0.606}$
(c) benzotriazole added	$C = 1.95 t^{0.506} \approx 1.95 \sqrt{t}$
(d) pure water, no irradiation	$C = 0.68 t^{0.240} \approx 0.68 \sqrt[4]{t}$

For (a) and (b) the exponent can in practice be put equal to 0.5, which means that a square root law¹⁰⁾ has been found. To support this approach mathematically, an attempt was made to derive the same law from the facts of radiolytic decomposition of water and reactions of these products with the copper surface.

In Chapter 2 it is said that hydrogen peroxide production in oxygen-saturated irradiated water is a linear function of the absorbed dose, but that a certain decomposition of hydrogen peroxide is catalyzed by copper(II) ions (produced by the reaction of H_2O_2 with a copper surface) and that the production rate of hydrogen peroxide decreases with increasing pH value or irradiation time. For this reason and because of the increasing Cu(II) concentration in solution the production rate of copper(II) ions should decrease with the irradiation time. This could be formulated as follows:

$$\frac{dC}{dt} = a \frac{1}{C^x} \quad (9)$$

where, a: constant,
t: irradiation time (h),
C: concentration of Cu(II) ions in solution,
x: 'reaction parameter' .

After integration, we find:

$$C^{(x+1)} = (x+1) a t \quad (10)$$

or

$$C = A t^{\frac{1}{x+1}} \quad (10a)$$

where, A is a new constant.

For the radiolytic oxidation of copper we assume a simple reciprocal proportionality of copper(II) ion production per time interval $\frac{dC}{dt}$ and copper(II) concentration in solution (C). In this case the 'reaction parameter x' will be 1 and Eq. 10a will lead to

$$C = A \sqrt{t} \quad (11)$$

For the corrosion of copper surfaces by demineralized oxygen-containing water ('normal' conditions) the surface reactions are much more complicated. The copper(II) ion production slows down much faster as a function of time than in the case of 'active oxidation' during irradiation probably because of a more stable equilibrium between oxygen and copper(II) ions in the solution on the one hand and the tube surface on the other. In this 'normal' case the reaction parameter x should be greater than 1. (It must be noted that the velocity of the circulating water was always kept constant.)

As it seems from case (d) the reaction parameter x for the 'normal' corrosion of copper surfaces by water circulating in a closed circuit approaches a value of 3, which confirms the more complicated surface reactions predicted for this case. It means that for 'normal' corrosion, i.e. absence of active oxidizing products of irradiation, a $\sqrt[4]{t}$ proportionality of the increase of copper(II) concentration can be assumed for conditions similar to those of the simulator 'background' experiments (4.3.1.1).

A further comparison of the straight lines in fig. 4 shows that the only difference between (a) and (c) consists of a different coefficient A , which could be interpreted as indicating that the benzotriazole-treated surface behaves as though it were a smaller surface. This interpretation is valid when we consider that the constant A is representative for all the parameters which were kept constant during the experiment, e.g. absorbed dose, temperature, water flow rate, copper surface, etc....

Case (b) as can be seen clearly from fig. 4, is not very well represented by the given equation. By decomposition and use of hydrazine the 'constant' A seems to change during the experiment so that the curve starts somewhat like that of case (b) but ends up at the level of case (a). This change of A could be expressed by the addition of two partly overlapping curves, which are valid for different time intervals and have a different coefficient A , but both have a \sqrt{t} increase of the copper(II) ion concentration. As pointed out above an explanation would be that all the hydrazine is consumed or decomposed after a certain period of irradiation and the solution later behaves like pure irradiated water. More complicated surface reactions leading to an x in eq. 10a not equal to 1 could be discussed as well as a change in the time dependence of the increase of the copper(II) concentration, but they seem to be less probable. The coefficients found for (c) are then more or less artificial and do not show the true outline.

To minimize the radiolytic corrosion in irradiated copper tubes the regular addition of benzotriazole to the water in a circuit is proposed. This extends the intervals between regeneration cycles from 3-4 days to at least 3 weeks. For new developments under similar conditions it is advisable to provide a place for the addition of benzotriazole, eventually with a built-in filter for the filtration of the insoluble parts of the commercial product, if the whole circuit is not constructed in another material (e.g., Al or stainless steel).

Further experiments on these effects particularly to learn more about the parameters hidden behind the constant A , will soon be carried out.

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FIGURE CAPTIONS

- Fig. 1 : Diagram of circuit-simulator.
The lines on top represent the 19 equidistant removable copper plates;
the arrows show the tube connections for water circulation and the
direction of flow.
- Fig. 2 : Present state of the CERN Synchro-cyclotron RF-cooling water circuit.
Water irradiation is possible near the D and C electrode as marked
by X.
- Fig. 3 : Copper(II) ion production (in mg/l) versus experimental time (in hours)
for experiments in the simulator.
The numbers indicate the curves referred to in the text.
- Fig. 4 : Logarithm of copper(II) ion production (in mg/l) versus logarithm of
experimental time (in hours) for experiments in the simulator.

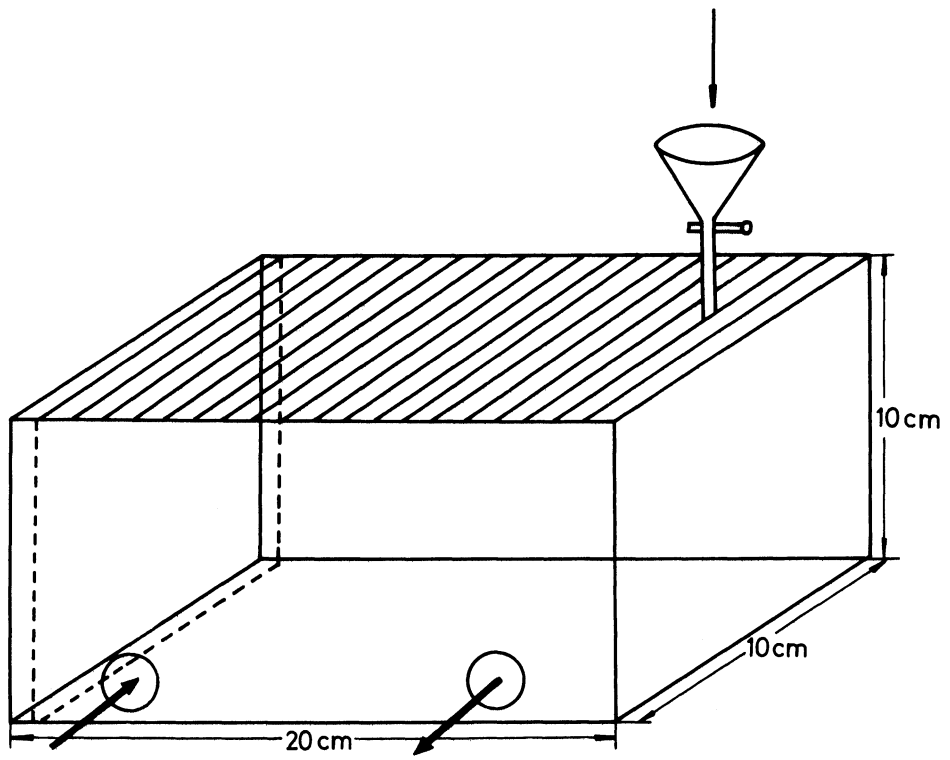


Fig. 1

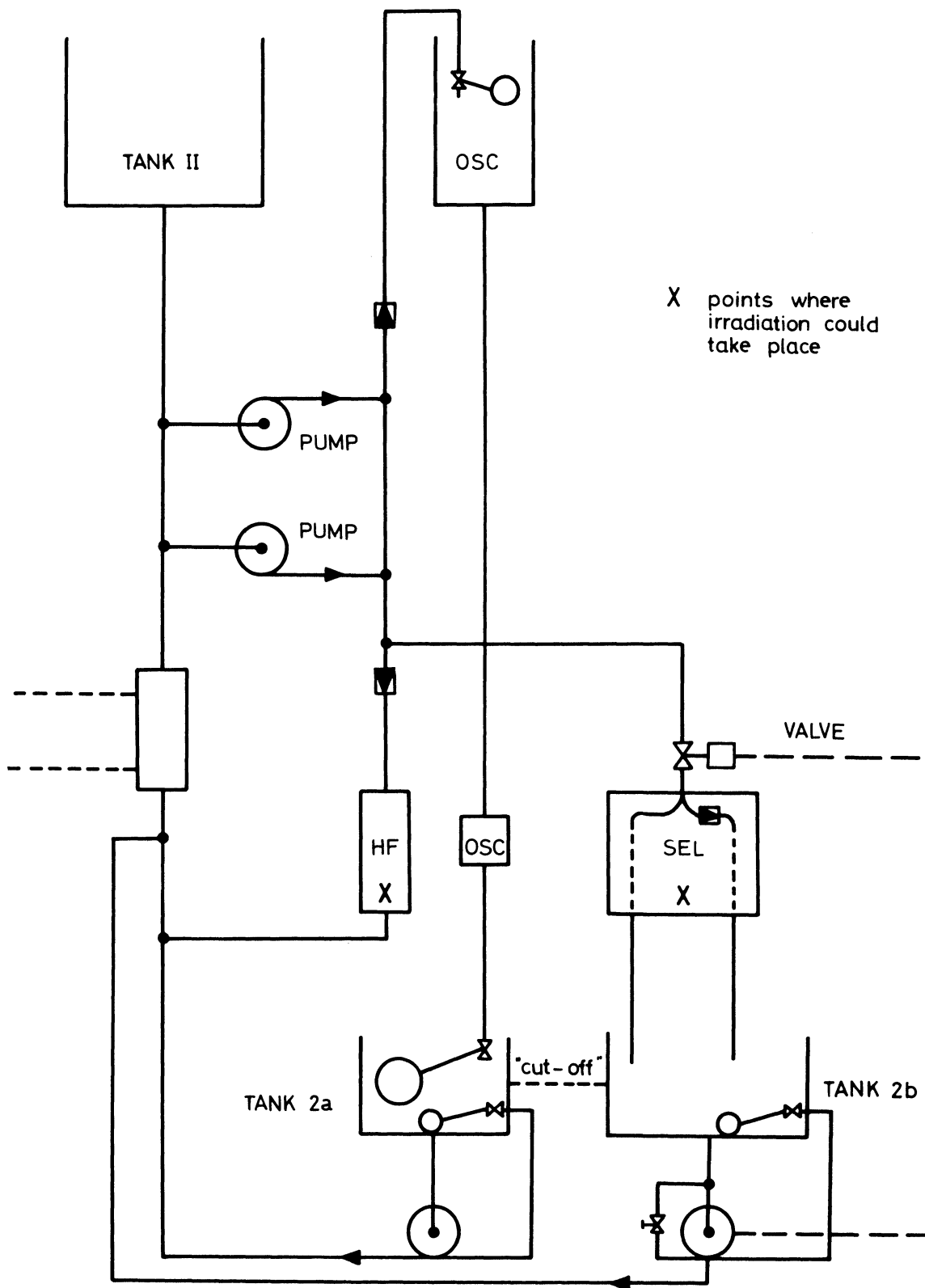


Fig. 2

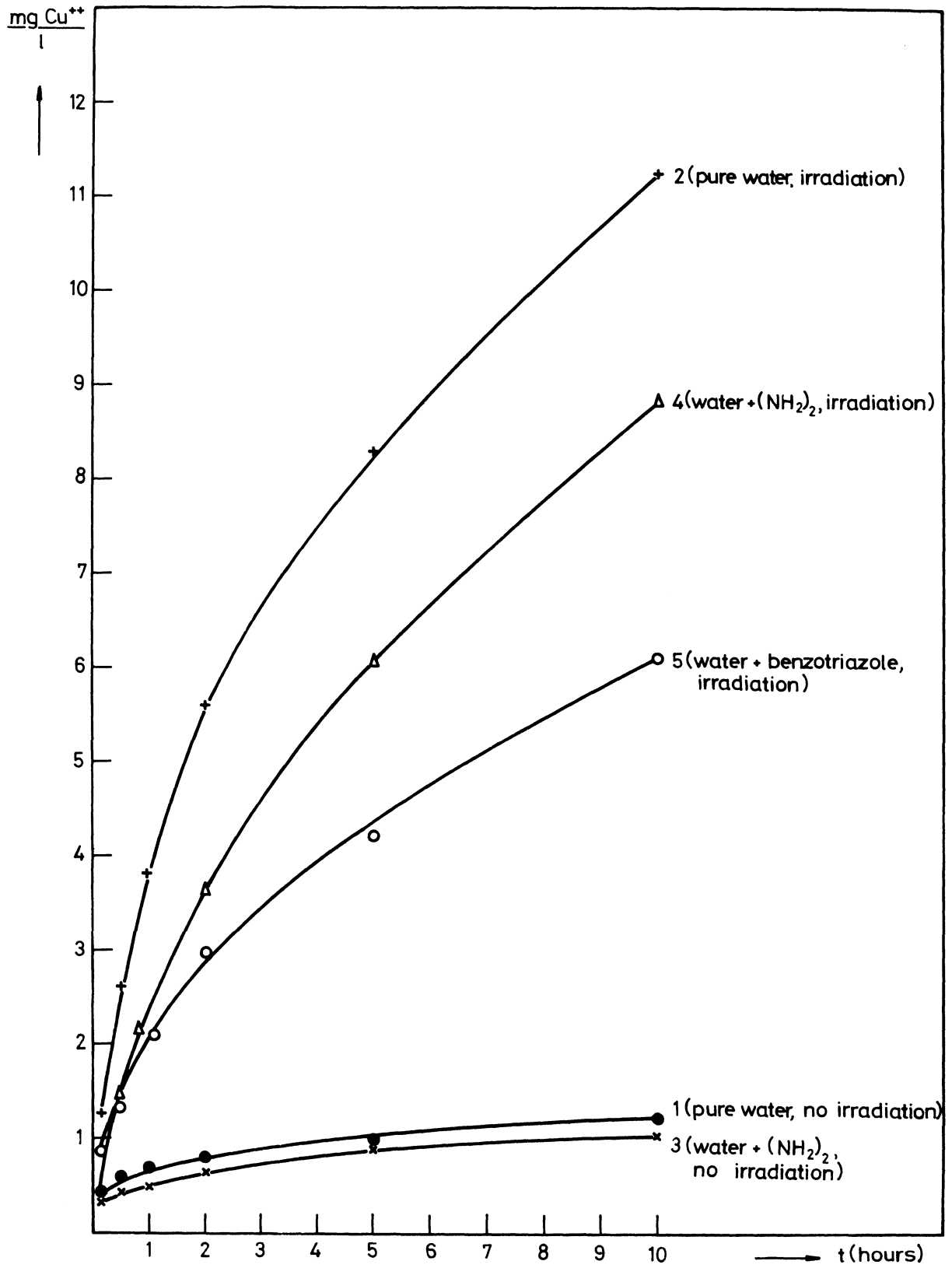


Fig. 3

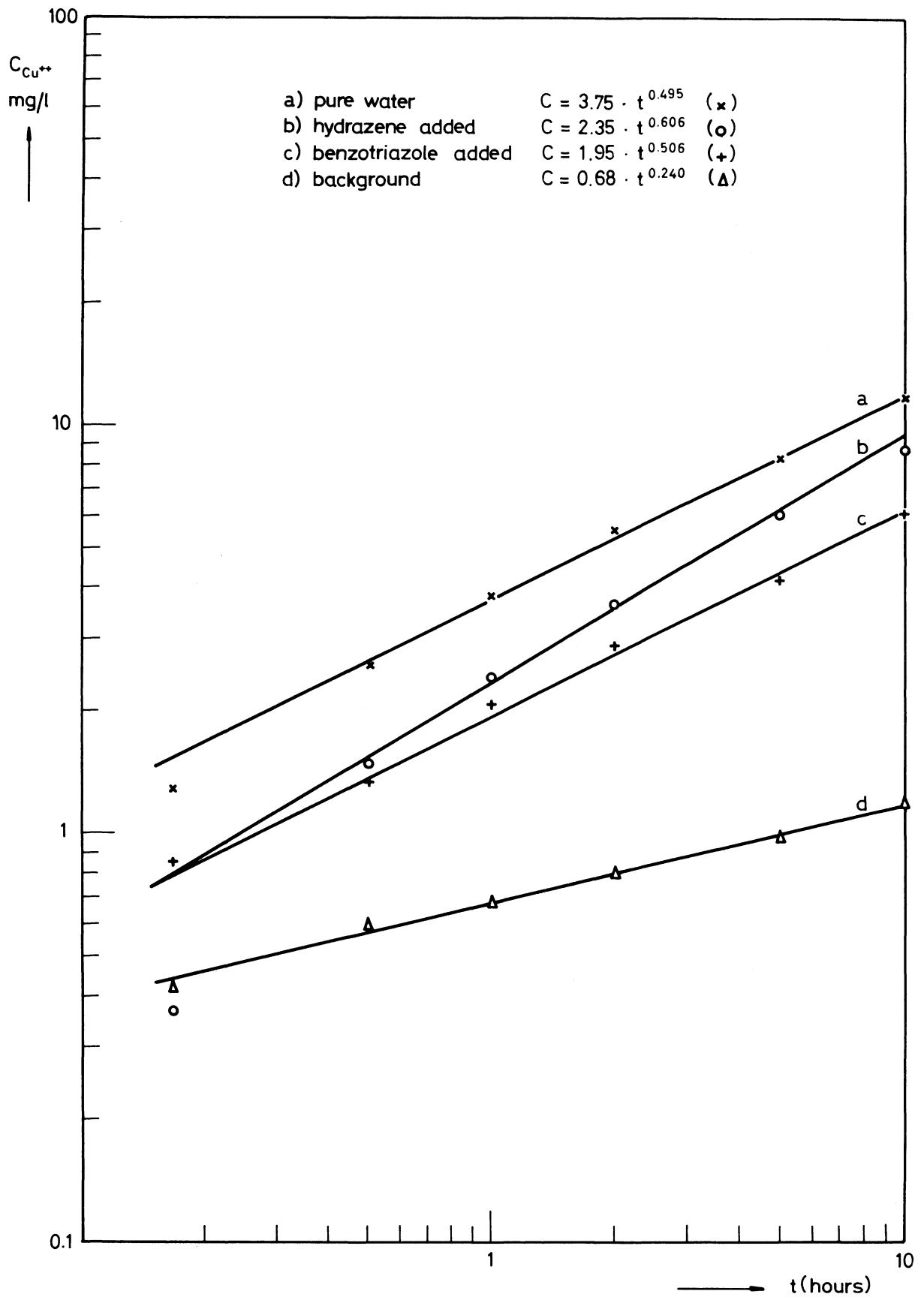


Fig. 4