

THE CHARACTERISTICS OF THE ELECTRONICS RAHBER WATER COOLER

Z.A. Khan and M. Zamin Hussain

National Physical and Standards Laboratory, Islamabad

(Received January 1, 1987; revised July 20, 1988)

The electronic Rahber water cooler, manufactured for decontaminating drinking water (against bacteria) by electrolysis using silver electrodes, is very likely to contaminate the drinking water with AgCl as a result of chemical action between the dissolving silver anode and the chloride ions in water particularly when the chloride ion is present to more than 10 mg/litre in the drinking water. Experiments also show that the silver anode is electrochemically oxidized to Ag₂O and AgO and that these oxides come off the electrode easily. Consequently, after a cooler has been used for some time, it is bound to contaminate the drinking water with silver oxides. The silver chloride and the oxides would generally not be visible because of their low concentrations under normal flow rates from a cooler.

Key words: Electronic water purifier, Decontamination device for drinking water, Electrolysis.

INTRODUCTION

The electronic Rahber water cooler, manufactured by Rahber Company under a Pakistan Patent [1], is fitted with two silver-strip electrodes in the passage of the tap of the cooler. The electrodes are connectable to a 3V battery kept in a pocket of the vessel. The electrical circuit is completed when the tap valve is opened to draw water from the cooler. In the absence of a battery, the necessary voltage can also be supplied from mains AC voltage through a rectifier (adopter). The quality of this cooler is that the bacteria in water gets killed while passing through the tap due to silver ions being released from the anode. The device thus purifies water for drinking purpose.

Since this device is for public use, it was of interest to investigate the effect of electrolysis on water apart from killing bacteria. The present investigation was undertaken for the said purpose. Drinking waters generally contain quite a few types of cations and anions. Apart from the reduction and oxidation of these ions, electrolysis of water giving rise to hydrogen and oxygen evolution (or oxide formation) at the cathode and anode are possible reactions. The various possible reactions and their thermodynamic potentials have been given in the literature [2]. Precipitation of silver chloride can also occur by chemical action between the silver ions (released from the anode) and the chloride ions present in drinking water. We focussed our work on the possible precipitation of silver chloride and to find out as to what really happens at the electrodes.

EXPERIMENTAL RESULTS AND DISCUSSION

It was of interest in the first place to approximately know the concentration of silver ions in water that is drawn

through the tap of the cooler under the conditions of electrolysis. Two coolers were available at our labs. One of them (we may call it No. 1) had been used more frequently than the other (No. 2 over the past two years. The cooler No. 2 was in fact out of use as it had developed a minor leak at the tap-cooler joint. Experiments were performed on the tap water of this laboratory at room temperatures which varied from 22 to 31° depending on the season. Measurements were made on both these coolers for silver and chloride ions on the issuing water. The electrodes from the cooler No. 2 were afterwards taken out for visually seeing the process of electrolysis. The experimental results will be described separately for the two types of experiments.

A. The determination of silver and chloride ions in water was made by use of ion-selective electrodes of the Orion Company of USA. A voltage of about 5 volts D.C. was applied to the electrodes of the coolers through an adopter.

It was found that the concentration of silver ions was dependent on the rate at which water was drawn from the coolers. The rate of draw could be controlled by the knob of the tap and rate of draw was measured by noting the time for a given volume drawn. Experiments were also conducted by opening the tap only slightly so that the electrical connections were made but no water flowed out of the tap. In such experiments the cooler was gently shaken in a swival way during electrolysis. Knowing the time of electrolysis and the volume of water in the cooler the time of electrolysis for one litre could be calculated. Since we only need to arrive at qualitative results, therefore, in reporting the results below, no distinction is made

in the two types of experiments and the results are reported in terms of the time in which one litre would be drawn. The results of experiments on different days were not reproducible. The reason for this, to some extent, seems to be that the ion-selective electrodes used for the determinations do not work satisfactorily for concentrations below 0.1 mg/litre and 8mg/litre for silver and chloride ions respectively; but the main reason looks to be the changing surface of the electrodes in the cooler. We shall see below in section (B) that the oxides do also come off the anode even without shaking the system. However, it may be mentioned that conclusions were drawn from a number of experiments and that the results were good enough for the purpose of drawing the conclusions that have been presented in this communication.

A typical result on the same day and same sample of tap water in cooler No. 1 showed the water to contain about 0.01, 0.05 and 0.09 mg/litre of silver ions when water was drawn from the cooler at the rate of one litre in 1, 7 and 12 minutes respectively. Similarly when water was drawn at the rate of one litre in 5 minutes, the chloride ion concentration decreased from 6.8 mg/litre (in tap water) to 4.8 mg/litre.

The silver ion concentrations were found to be generally higher when water was drawn through cooler No. 2. For example, concentrations of silver ions were found to be 0.08 and 0.16 when the draw rates for one litre were 1.5 and 1.9 minutes. The corresponding chloride ion concentrations were found to be 8 and 5.5 mg/litre respectively (the corresponding chloride ion concentration in tap water was 8.8 mg/litre). It may be mentioned that chloride ion concentrations in tap water was found to vary from 6 to 10 mg/litre from day to day.

Before we draw conclusions from the above, it may be mentioned that for the same D.C. voltage (applied through the adopted) the currents in cooler No. 1 and No. 2 were about 500 mA and 20mA respectively. Another factor which may be mentioned is that silver chloride has very little solubility [3]. Calculations have shown that at 25°, for a water containing 8 mg/litre of chloride ions, a concentration in excess of 0.07478 mg/litre of silver ions will cause precipitation of silver chloride (the solubility product of AgCl is 1.56×10^{-10} at 25°). If the whole current at the anode of the cooler were to produce silver ions, then only about 1.1 mA would be sufficient to generate 0.7478 mg of silver ion in one minute. It may be mentioned in passing that the recommended concentration of silver ions is 0.05 mg/litre which is quite likely to cause precipitation of AgCl because drinking waters may contain much higher amounts of chloride ions than 8 mg/litre for which cal-

culations have been shown here in view of the water at this laboratory. The tolerable limit [4] of chloride ion in drinking water is 200 mg/litre. For precipitation conditions please also see section (B) below.

In view of the experimental results and the other considerations mentioned above, we conclude the following:

(i) The concentration of silver ions depends on the rate at which water is drawn through the tap. Slower the drawing rate, greater is the concentration. However the concentration may not be a direct function of time (for drawing same volume) as precipitation of AgCl and other factors (changes in the ratio of the current consumed for various reactions occurring at the anode are involved).

(ii) The concentration of chloride ions in water tends to decrease partly because of AgCl precipitation in the bulk of water and partly because of anodic oxidation of the ion at the anode to form silver chloride.

(iii) Although the current in cooler No. 1 was much higher than in cooler No. 2 yet the concentration of silver ions was found to be higher in samples drawn from cooler No. 2. This shows that the rate of anode dissolution is dependent on the anode condition. The anode in cooler No. 1 must have been more thickly oxidised due to its long use.

(iv) The concentration of silver ions in water samples drawn from coolers is much smaller as compared to the current. This shows that most of the current goes in oxidising the silver anode. And in view of (iii) it looks that as the oxide film grows thicker, comparatively more current goes in oxide formation than in anodic dissolution of silver.

B. In order to see things visually, the electrodes from cooler No. 2 were taken out of the tap. The anode was found to be covered by a film which had patches of grey black, grey brown and white colour. The cathode also had a sort of darkish colour. The electrodes were about 3.5 cm long and 1.0 cm broad. Short leads for electrical connections were soldered at one end of the electrodes. The electrodes were cleaned with emery paper. The electrodes were tied together at the connection ends after giving small packing of rubber in between them. The packing was given only to about 1/3rd of the length of electrodes. The distance between the electrodes was kept about 0.5 to 0.7 cm (the distance between electrodes in the cooler is about 3 to 4 mm). Freshly cleaned electrodes were dipped in each of the following experiments to about half the length. The volume of samples used in electrolysis was about 60 ml taken in a 100 ml beaker. A battery of 3 V was used for

electrolysis. An ammeter was connected in series to read the current.

(i) In tap water (conductivity 630 micromhos; PH- θ), the current was observed to be about 4 mA during the whole 2 hour period of the experiment. Hydrogen gas bubbles started rising from the cathode almost as soon as the electrical connections were made. After about 10 seconds of electrolysis a white colloidal precipitate was observed to start forming in the vicinity of the anode. This precipitate continued to form, fall downwards and spread into the bulk of water. After about 7 minutes, the anode was observed to start turning greyish black and greyish material started coming into solution as a fine powder. It may be mentioned that no gaseous evolution was observed at the anode. The colour of the cathode did not change much. The whitish precipitate in the solution continued to be formed for quite some time but the black material coming off from the anode eventually made the whole solution blackish. The electrodes were taken out after about two hours. The anode was found to be black whereas the cathode had turned only slightly dark. The water sample was turbid and dark in colour and some brown black and greyish black particles were found at the bottom of the beaker. The obvious conclusion from these observations (as to the white precipitate) would be that the silver ions produced from the anode precipitate the chloride ions present in water. It may be mentioned that since silver ions diffuse only slowly, the concentration of silver ions would surpass the solubility product of silver chloride much quicker (than we may expect) in the vicinity of the anode, i.e. precipitation will start in the vicinity of anode much before we produce enough silver ions to reach the solubility product considering the whole water in the container. It may be mentioned here that in a separate experiment done previously with tap water and using 5V supply, we had observed the anode to first turn brownish grey and then blackish (apart from the formation of white precipitate of AgCl). It is obvious that the brownish and greyish black films are due to Ag_2O and AgO respectively [3]. We also observed that if the electrolysis was discontinued when only white precipitate was being formed, the solution turned to purple blue when exposed to sun light. This was obviously due to photochemical decomposition of silver chloride [5].

It may also be mentioned that darkening of the cathode to some extent and occasionally a whitish film with sometimes a greenish tint were also observed at either or both the electrodes. For this, various electrochemical and absorption type reactions are possible because tap waters contain a variety of materials.

(ii) In order to conduct electrolysis in water having negligible chloride ions, experiment was conducted in distilled water to which a few drops of diluted Analar H_2SO_4 had been added. The pH of this solution was about 4 and the conductivity was about 640 micromhos. In this solution it was observed that white precipitation did not occur even upto 30 minutes after starting electrolysis (the current was about 5 mA). This showed clearly that the white precipitate mentioned in (i) above was due to formation of AgCl. The formation of oxides on anode were observed however the falling out of these oxides was at a much less rate than observed in case of tap water. One interesting thing observed in this electrolysis was the accumulation of a fluffy white and shiny material around the cathode. This material was obviously not an oxide of silver. It showed no test for sulphate ions and gave positive tests for silver. The obvious conclusion that we made was that the silver ions, produced at the anode, migrated to the cathode where they were discharged to form metallic silver. Because of the hydrogen evolution at the cathode, the silver atoms (discharged silver ions) could not settle down in the lattice of the cathode. It may however be mentioned that formation of metallic silver and its coming into drinking water, during normal use of the cooler, is very unlikely because in that case water would be flowing in a particular direction and the silver ions would have little chance to reach the cathode.

(iii) Results in distilled water made alkaline with a few drop of Analar NaOH were similar to the above, i.e. H_2 bubbles were observed at cathode but no oxygen evolution at the anode, and that brownish to blackish films are formed at anode which come off as fine powders (suspensions) in water. The above experiments indicate that in the normal use of the coolers, silver chloride precipitation is very likely and that the oxides of silver are also bound to come out in the drinking water.

Acknowledgement. The authors would like to thank Dr. S.S.H. Zaidi, Director, National Physical and Standards Laboratory for kindly providing the laboratory facilities. The authors would also like to thank Mr. Shaukat Inam and Mr. Mohammad Fayyaz for their assistance in the experimental work.

REFERENCES

1. M.A.A. Beg, M.A. Rashid, M.A. Siddique, S.N. Mohmood and A.H.K. Youssufzai. "A process for the Production of a Rapid Water Decontaminating Device (Electronic Water Purifier)". Pakistan Patent No. 1 2717.

2. W.M. Latimer *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions* (Pub. Prentice Hall, Inc.), 2nd ed.
3. *Handbook of Chemistry and Physics*, Weast (CRC Press, 1980-81), 61st ed.
4. W.H.O., *Drinking Water Standards*.
5. I.M. Kolthoff *Quantitative Chemical Analysis et al.* (Pub. Macmillan Co.).