Electrochemical antiscaling treatment using a fluidized bed

M. Marchesiello[a,*], P.-X. Thivel[a,b,c,*]

[a] Univ. Grenoble Alpes, IUT 1, F-38000 Grenoble, France
[b] Univ. Grenoble Alpes, CNRS, Grenoble INP[1], LEPMI, 38000 Grenoble, France
[c] Univ. Savoie Mont Blanc, LEPMI, 73000 Chambéry, France

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ABSTRACT

A new kind of electrochemical antiscaling device using a fluidized bed constituted of 1 mm in diameter 316 stainless steel balls was investigated. The presence of the fluidized bed between the two electrodes substantially increased the antiscaling power of the device of nearly 90%. The balls act as bipolar electrodes where the anodic and cathodic electrochemical reactions responsible of the antiscaling properties also took place, allowing a treatment in the entire volume of the water. The influence of current density, operating time and height of the fluidized bed (or electrode surface area) on the efficiency of the device was studied.

1. Introduction

Undesirable scale deposits on industrial or domestic equipments and water distribution networks can lead to important technical and economical consequences (obstruction of pipes, heat transfer reduction, seizing of valves, clogging of filters…). Scaling is often observed on hot surfaces in contact with water (heat exchangers, water heater, household appliances, hot water pipes…), but can also appear on surfaces further to water aeration (when water enters reservoirs for example) or pH increase (for example when bleach is added for disinfection purposes).

Scale is mainly composed of calcium carbonate $CaCO_3$ the precipitation of which results from the following reaction:

$$Ca^{2+} + CO_3^{2-} = CaCO_3 \tag{1}$$

This reaction which can occur as soon as the product of Ca^{2+} and CO_3^{2-} concentrations is higher than the $CaCO_3$ apparent solubility product K's (namely the solubility product expressed with the concentrations of the species involved, not with their activity) depends on the following equilibriums:

$$CO_2\,atmospheric + H_2O = H_2CO_3 \tag{2}$$

$$H_2CO_3 + H_2O = HCO_{3-} + H_3O^+ \tag{3}$$

$$HCO_3^- + H_2O = CO_3^{2-} + H_3O^+ \tag{4}$$

The saturation rate of the water as regards calcium carbonate precipitation can be defined as following [1]: t= [Ca²⁺]. [CO₃²⁻] /K's.

The saturation rate t indicates the discrepancy existing between the real water state and the equilibrium state between Ca^{2+}, CO_3^{2-} and $CaCO_3$, called "calcium-carbonate" equilibrium [1]. When t = 1, the water is in equilibrium with respect to calcium carbonate. If t < 1, the water is considered to be "aggressive". This means that, thermodynamically, it is liable to dissolve calcium carbonate. In contrast, if t > 1, the water is said to be "calcifying", indicating that, thermodynamically, it is capable of precipitating calcium carbonate, the tendency to precipitation being all the more pronounced that t is high [1]. In this latter case, treatments to avoid scale deposits are often necessary. They can be separated in two categories:

- Chemical treatments (examples lime addition in the chemical decarbonation process leading to $CaCO_3$ precipitation and its elimination by sedimentation, sulfuric acid addition to lower pH below the saturation pH of the water).
- Physical treatments which involve a physical principle without chemical addition: electrochemical treatments [2–7], magnetic treatments [8–14], ultrasonic treatments [15].

Physical treatments are simplest to apply and generally affect the calcium carbonate germination-growth process [16]. The homogeneous germination step is enhanced in treated water. As a consequence, a decrease in adherent deposits resulting from heterogeneous precipitation is observed during subsequent use of water (usually when water is heated) [2,4].

However as physical treatments usually do not modify substantially water chemical composition (pH, hardness, alkalinity…), their effectiveness was, in the past, difficult to prove and therefore they were

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considered with suspicion. During the last thirty years many different accelerated evaluation methods were developed [17] to show beyond doubt the effectiveness of physical treatments by testing water before and after treatment, and also to classify waters with regard to their scaling power.

All these accelerated evaluation methods have their advantages and drawbacks and their complementarity is useful for scaling phenomenon forecasts in real industrial or domestic equipments and water distribution networks. They can be classified in electrochemical methods (using chronoamperometry [4,18,19], chronoelectrogravimetry [19,20], impedance technique [19]) and non electrochemical methods (critical pH method [21], thermal methods [22], evaporation method [4], methods based on CO_2 degassing [23,24]).

Among the physical treatments, electrochemical antiscaling treatments have been widely studied and proved to be effective [2–4]. The devices present two electrodes usually made of an inert material regarding the flow of current. The cathode is generally made of stainless steel [2–4], while the material chosen as anode can be stainless steel [2], iridium titanium [3], titanium [4].

On these inert electrodes the anodic and cathodic reactions correspond to the oxidation and reduction of water:

$$\text{Anode:} H_2O = 1/2 O_2 + 2H^+ + 2e^- \tag{5}$$

$$\text{Cathode:} 2H_2O + 2e^- = H_2 + 2OH^- \tag{6}$$
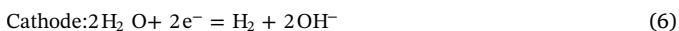
On the cathode another reaction can occur, i.e. the reduction of dissolved oxygen:

$$1/2 O_2 + H_2O + 2e^- = OH^- \tag{7}$$

If the anode is made of an oxidable metal, a dissolution of the metal will take place with production of cations that can act as coagulants in the case of iron or aluminium electrode [25]. The resulting iron or aluminium hydroxides formation promote $CaCO_3$ homogeneous precipitation in water and besides this phenomenon has led to antiscaling devices [26].

Fig. 1 shows the succession of the chemical reactions taking place in water as a result of the electrochemical reactions. Following the production of OH^- ions at the cathode, carbonic acid H_2CO_3, always presents in natural water, turned into bicarbonate ions HCO_3^-. As pH continues to increase HCO_3^- ions lead to carbonate ions CO_3^{2-}. The product of Ca^{2+} and CO_3^{2-} concentrations can then locally reach and exceed the apparent solubility product K's (if the water was originally aggressive, t < 1). If the water was originally calcifying (t > 1) a local increase of the saturation rate t will occur at the vicinity of the cathode, enhancing the ability of water to precipitate calcium carbonate: OH^- concentration near the cathode can be sufficiently high to raise the water pH until the homogenous germination of $CaCO_3$ crystals appears in the solution. However the heterogeneous precipitation of calcium carbonate that can also take place on the cathode must be avoided because the resulting scale deposit on the electrode would block the electrochemical process. pH decreases at the vicinity of the anode if the electrode is made of an inert metal because of H^+ production following Eq. (5): no precipitation of $CaCO_3$ can then appear on the anode. Protons production leads to the formation of carbonic acid H_2CO_3 from HCO_3^- (Fig. 1).

Overall, the current flow through the water doesn't modify substantially the following chemical parameters: pH, hardness and alkalinity. This can be explained by the recombination between a significant part of CO_3^{2-} and/or $CaCO_3$ formed near the cathode and H_2CO_3 formed at the vicinity of the anode with HCO_3^- reappearance in the water (Fig. 1). However $CaCO_3$ crystallisation seeds seem to persist in treated water and further contribute to reduce substantially the amount of adherent scale on hot walls in contact with water [2]. The appearance of non adherent $CaCO_3$ sludge is evidenced and this sludge can easily be removed by blowdowns of the containers where the water is heated [4].

The aim of the present study was to investigate the effectiveness of a new kind of electrochemical antiscaling device using a fluidized bed constituted of 1 mm in diameter 316 stainless steel balls. 316 *stainless* steel was chosen because of its superior corrosion resistance and oxidation behavior compared to 304 *stainless* steel. Three-dimensional electrodes, as fixed bed or fluidized bed, where electrochemical reactions are generated, are already used for a wide range of applications like metals removal and water treatments [27,28]. But, to our knowledge no electrochemical apparatus using a fluidized bed was already used as antiscaling device. During fluidization, the 316 *stainless* steel balls are located between two electrodes also made of 316 *stainless* steel being in the electric field, the balls should act as little bipolar electrodes where both anodic and cathodic reactions occur leading to an increase of OH^- production in the entire volume of the solution between the two electrodes. The quantity of $CaCO_3$ germs would normally increase leading to better antiscaling properties of treated water. Further more the abrasive action of the balls on the cathode should contribute to the removal of any $CaCO_3$ deposit at the cathode resulting from the heterogenous precipitation of calcium carbonate.

2. Materials and methods

2.1. Water

Grenoble tap water which was used as test solution to check the effectiveness of the treatment is from the alluvial ground water fed by the Drac river. Its physicochemical characteristics are presented in Table 1: it presents a total hardness of about 4 méq/L, a total alkalinity of about 3 méq/L. At 15 °C (temperature during the electrochemical treatment) Grenoble tap water is slightly oversaturated with respect to $CaCO_3$ (slight tendency to precipitate $CaCO_3$ with a saturation rate of t = 1.2). In absence of water aeration or pH increase, scale is rarely observed on cold surface. However the saturation rate increasing with temperature, the risk of heterogeneous precipitation on hot surfaces is important and all the more pronounced that the temperature is high.

2.2. Experimental set-up

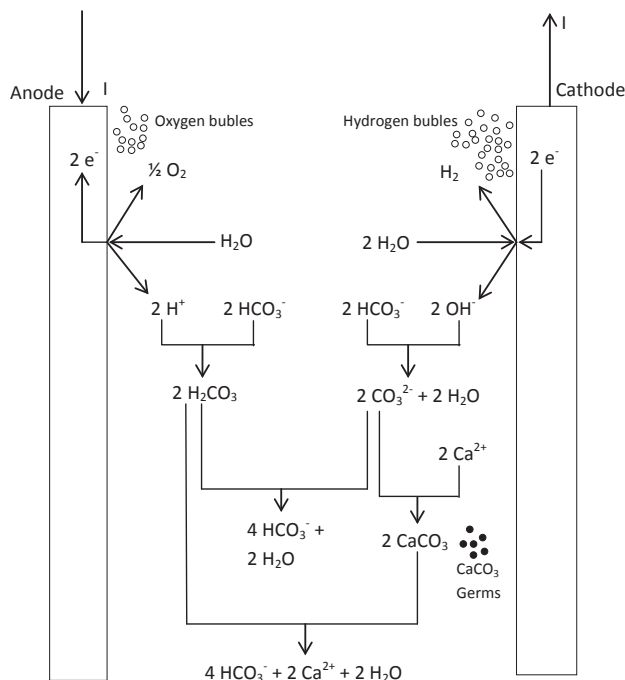The experimental set-up is presented in Fig. 2a. The electrochemical

Fig. 1. Electrochemical and chemical reactions taking place during the water treatment.