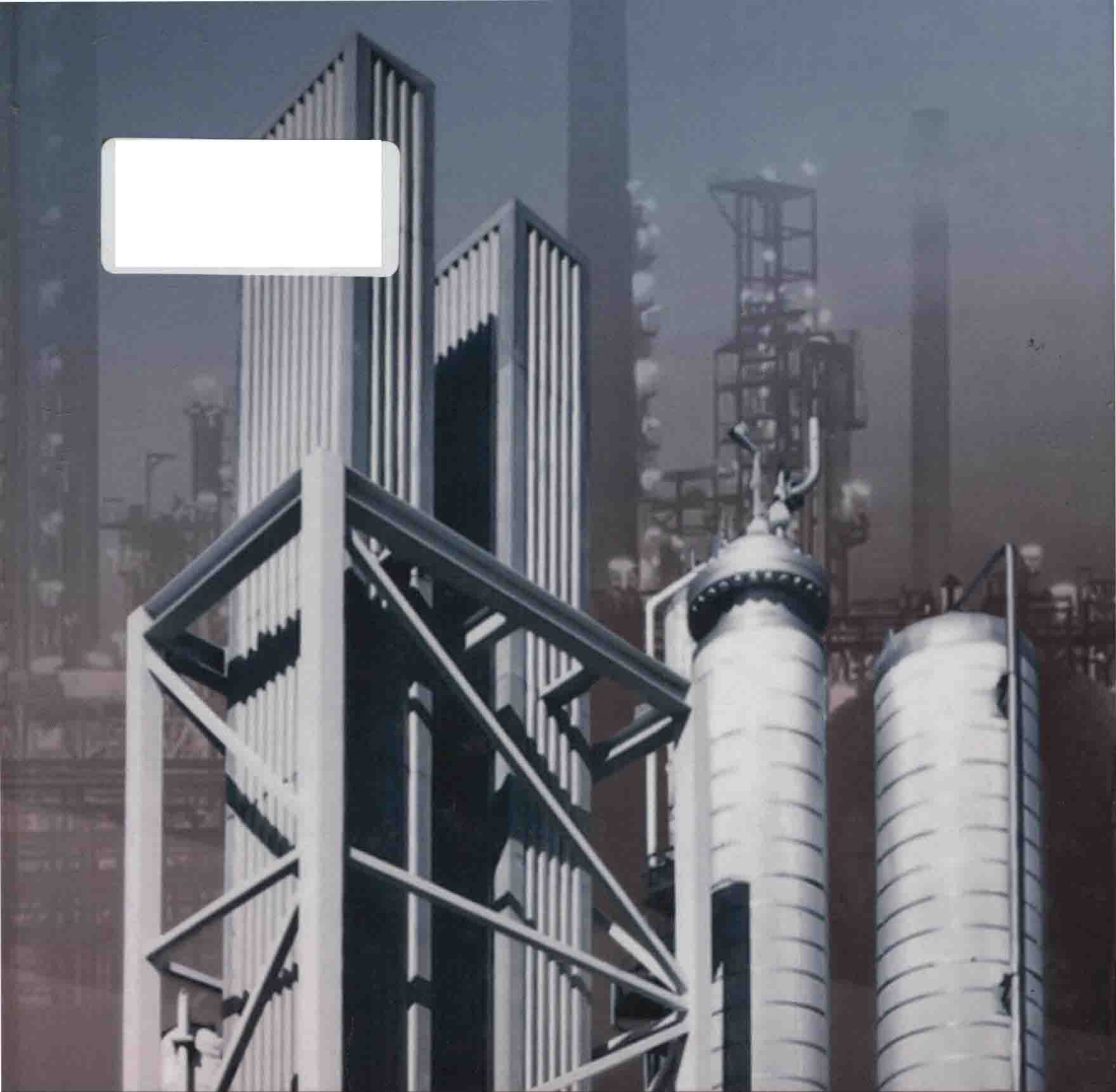

Advances in

OIL AND GAS INDUSTRY

Jane Urry

Advances in Oil and Gas Industry

Edited by **Jane Urry**

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Preface

This book discusses the latest advances in the field of oil and gas industry. Oil and gas are the most crucial non-renewable sources of energy. The tasks of producing, managing and exploring these resources in accordance with HSE standards are challenging. Therefore, it becomes important to discover and implement novel technologies, procedures and workflows. This book discusses some of these themes and presents certain enhanced technologies associated with the oil and gas industry from HSE to field management concerns. Novel technologies for digital rock physics, geo-modeling and transient well testing have also been highlighted in this all-inclusive book. The aim of this book is to serve as a great source of information for engineers, geoscientists, researchers and practitioners engaged in the petroleum industry.

After months of intensive research and writing, this book is the end result of all who devoted their time and efforts in the initiation and progress of this book. It will surely be a source of reference in enhancing the required knowledge of the new developments in the area. During the course of developing this book, certain measures such as accuracy, authenticity and research focused analytical studies were given preference in order to produce a comprehensive book in the area of study.

This book would not have been possible without the efforts of the authors and the publisher. I extend my sincere thanks to them. Secondly, I express my gratitude to my family and well-wishers. And most importantly, I thank my students for constantly expressing their willingness and curiosity in enhancing their knowledge in the field, which encourages me to take up further research projects for the advancement of the area.

Editor

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Section 1

HSE

Chapter 1

Electrolytic Treatment of Wastewater in the Oil Industry

Alexandre Andrade Cerqueira and Monica Regina da Costa Marques

Additional information is available at the end of the chapter

1. Introduction

Industrial development in recent decades has been a major contributor to the degradation of water quality, both through negligence in treatment of wastewater before discharge into receiving bodies and accidental pollutant spills in aquatic environments [1].

The importance of oil to society is unquestioned. It is not only a major source of energy used by mankind, but its refined products are the raw material for the manufacture of many consumer goods [2].

A world without the amenities and benefits offered by oil would require a total change of mindset and habits among the population, a total overhaul of the way our society works. At the same time, the oil industry is a major source of pollutants that degrade the environment, with the potential to affect it at all levels: air, water, soil, and consequently, all living beings on the planet [2].

Oil and its derivatives are the most important pollutants, due to, among other factors, the increasing amounts that have been extracted and processed. Also, carelessness and neglect of safety standards and routine maintenance of equipment (pipelines, terminals, platforms) aggravate the water pollution problems caused by the oil industry [3].

Due to the negative environmental impacts of exploration and production of oil, new more restrictive environmental laws and regulations have been issued. It is estimated that in the United States alone, the oil industry will need to invest about 160 billion dollars in actions to protect the environment over the next 20 years to meet environmental legislation more demanding than currently adopted in Brazil [4].

One of the crucial points to be attacked is the issue of water production, which is generated in this activity, which is increasing in volume as they get older wells and new wells are drilled [5]. On average for each m^3/day of oil produced, 3-4 m^3/day of water is produced, although this figure can reach up to 7 m^3/day or even more in exploration, drilling and production. The water produced along with oil corresponds to 98% of the effluents. It contains salts, oils and other toxic chemicals in addition to having high temperature and no oxygen [6].

According to [7], treatment of produced water is an urgent matter in view of the high daily volume. Different processes have been described for the treatment of such effluent, but the most frequently used are chemical destabilization [8,9] and electrochemical destabilization [10,11]. Biological processes are rarely used since these effluents usually contain biocides [12].

The use of EF can enable the release into receiving bodies or reinjection in wells of the treated effluent by reducing the organic load and removing oily and solid particles in suspension [13].

According to [14], the current EF technology inherently involves the formation of an impermeable oxide layer on the cathode and deterioration of the anode due to oxidation. This leads to loss of efficiency of the electroflocculation unit. These limitations of the process have been decreased to some extent by the addition of parallel plate electrodes in the cell configuration. However, the use of alternating current in EF retards the normal mechanisms of electrode deterioration that are inherent in DC system due to cyclical energization, thus increasing the electrode life.

In the present text, we evaluate the efficiency of electroflocculation with direct current and variable frequency alternating current with the use of aluminum electrodes for the treatment of oily wastewater from actual production.

1.1. Petroleum exploration and production

Petroleum is the name given to natural mixtures of hydrocarbons, which can be found in the solid, liquid or gaseous state depending on the conditions of temperature and pressure [15].

Oil is a combination of carbon and hydrogen molecules and is less dense than water, with a characteristic odor and color varying from black to brown. Although the subject of much discussion in the past, today oil's organic origin is accepted. Oil exploration and production is one of the most important industrial activities of modern society and its derivatives have many industrial applications. Because of the need to meet the growing demand for the product, the extraction of oil has increased greatly in recent decades. However, this extraction to meet world oil demand causes damage to the environment, with the main culprit being produced water [16,17].

1.2. Oily water

Oily water is a generic term used to describe all water which contains varying amounts of oils and greases in addition to a variety of other materials in suspension. These can include sand, clay and other materials, along with a range of dissolved colloidal substances, such as detergents, salts, metal ions, etc. To meet environmental standards for disposal and/or the characteristics necessary for reuse, the treatment of oily water can be complex, dependent on highly efficient processes.

In the petroleum industry, oily water occurs in the stages of production, transportation and refining, as well as during the use of derivatives. However, the production phase is the largest source of this pollution. During the production process, oil is commonly extracted along with water and gas. The associated water can reach 50% of the volume produced, or even approaching 100% at the end of the productive life of wells. The discharge or reinjection of this co-produced water is only permitted after removal of oil and suspended solids to acceptable levels [18].

The terms "produced water," "petroleum water", "formation water" and "oily water" are used to refer to the water extracted along with oil [17,19].

The composition of this produced water is very complex. Depending on its origin it can contain a wide variety of chemicals such as organic salts, aliphatic and aromatic hydrocarbons, oils and greases, metals, and occasionally radioactive materials. A striking feature of the water coming from offshore oil is its high salinity [17, 20, 21], which expressed as chloride ions (Cl^-) can reach 120 g/L [22].

In oil wells under the seabed, the amount of this wastewater can reach 90% of all effluent during the production of oil and can be 7-10 times higher than the oil extracted from a given well [17, 21].

A new oil field produces little oily water (about 5-15% of the total oil produced). However, as the well becomes exhausted, the water volume can increase significantly, to the range 75-90%. This excessive production of water has become a major concern in the oil and gas industry [23]. Before disposal into receiving bodies or use for re-injection into wells, it is necessary to treat this water because the large amounts of pollutants cannot be discharged into the marine environment [24].

1.3. Electrocoagulation

EC is a process that involves the generation of coagulants "in situ" from an electrode by the action of electric current applied to these electrodes. This generation of ions is followed by electrophoretic concentration of particles around the anode. The ions are attracted by the colloidal particles, neutralizing their charge and allowing their coagulation. The hydrogen gas released from the cathode interacts with the particles causing flocculation, allowing the unwanted material to rise and be removed (Figure 1). Various metals have been tested as electrodes, such as aluminum, iron, stainless steel and platinum [25].

The theory of EC has been discussed by several authors, and depending on the complexity of the phenomena involved can be summarized in three successive stages of operation:

a. Formation of a coagulating agent through the electrolytic oxidation of the sacrificial electrode, which neutralizes the surface charge, destabilizes the colloidal particles and breaks down emulsions (coagulation – EC step);
b. the particle agglutination promoted by the coagulating agent facilitates the formation and growth of flakes (flocculation – EF step) and,
c. generation of micro-bubbles of oxygen (O_2) at the anode and hydrogen (H_2) at the cathode, which rise to the surface and are adsorbed when colliding with the flakes, carrying the particles and impurities in suspension to the top and thereby promoting the clarification of the effluent (flotation – electroflotation step).

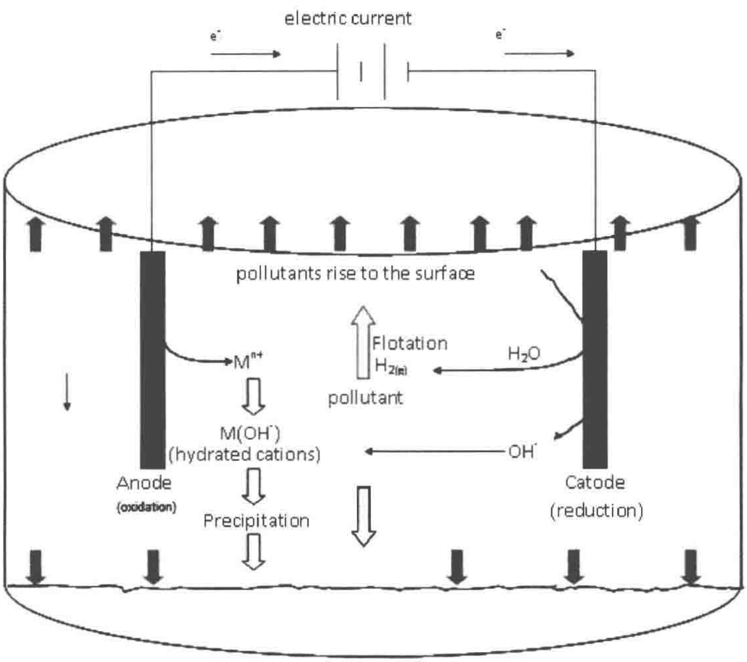

Figure 1. Schematic diagram of an electrocoagulation cell with two electrodes. Source: Adapted from [26].

Processes for electrochemical treatment of effluents have been described in the literature since 1903. In recent years interest has been growing, especially because of its simplicity of operation and application to treat various types of effluents from various sectors, such as domestic sewage [27], laundries [29], restaurants [30] steel mills [31], textile mills [32], and tanneries [33], facilitating the removal of metal ions [28], fluoride ion [34], boron [35] and oils [7, 36-41].

Several types of reactors have been proposed in the literature: monopolar, bipolar etc. But the most widely used is the monopolar reactor [14]. In its simplest form, a monopolar EF reactor is composed of an electrolytic cell with an anode and a cathode. In this case, large-area electrodes must be used, or electrodes connected in parallel. In the parallel arrangement, the electric current is divided among all the electrodes in relation to the resistance of individual cells. Thus, a lower potential difference is required in connection of this type when compared to a series arrangement.

For electrodes in series, a higher potential difference is required for a given current flow, because the electrodes are connected in series and have a higher resistance. The same current, however, runs through all the electrodes, and the current is divided among all the individual electrodes of the cells [14].

In the case of the bipolar reactor, the sacrifice electrodes are placed between the two electrodes in parallel (called conductive plates), without any electrical connection. Only two monopolar electrodes are connected to the power source, with no interconnection between the sacrifice electrodes. When the current passes through the two parallel electrodes, the neutral sides of the plate acquire an opposite charge than monopolar electrode. The external electrodes are monopolar and the internal ones are bipolar.

According to [42], most of the setups for treatment of effluents, the electrodes are made of identical material, mainly due to the following reasons:

- equal electrodes, made of the same material, have the same electrode potential;
- electrodes of different materials imply the use of materials other than iron or aluminum, which increases the cost;
- electrodes of the same material suffer the same wear, which simplifies their replacement.

In any electrochemical process, the electrode material has a significant effect on the effluent treatment. For the treatment of drinking water, it should be nontoxic, have low cost and be readily available [31].

Generally, however, iron electrodes have the disadvantage that the effluent has a pronounced green or yellow color during and after treatment. This coloration comes from the Fe^{2+} (green) and Fe^{3+} (yellow) generated in the electrolytic treatment. In contrast, with aluminum electrodes the final effluent is clear and stable, with no residual coloring.

In the work presented by [43], when aluminum and iron electrodes were tested under the same conditions, using direct current, the results for COD, turbidity and suspended solids were better for the aluminum than the iron electrodes. This advantage was also observed by [30]. However, when comparing the removal of arsenic by iron and aluminum electrodes, [31] found that the iron electrode was better because it showed 99% removal to 37% for aluminum. This difference was explained because the adsorption capacity of the $Al(OH)_3$ + by As^3 is much smaller than that of $Fe(OH)_3$.

Tests carried out by [44] of COD, phenols and turbidity of hydrocarbons from a petrochemical plant, using iron and aluminum electrodes, showed better performance by aluminum electrodes.

According to [45], just as in electrocoagulation, the removal of pollutants closely depends on the size of the bubbles generated, while energy consumption is related to the electrolytic cell design, electrode materials, arrangement of electrodes and operating conditions, such as current density, conductivity of the effluent and electrolysis time, among others. The difference in size of the bubbles in the effluent depends on the pH, current density, electrode material and surface condition of the electrodes.

The mechanism of EC is highly dependent on the chemistry of the aqueous medium, especially conductivity. Moreover, other characteristics such as pH, particle size and concentration of the constituents will influence the electrocoagulation process [14].

In an EC reactor, the rate of coagulant addition is determined by the kinetics of the electrodes. The reactions at the electrodes are heterogeneous and take place in the interfacial region between the electrodes and the solution. Since the reaction consists of electron transfer via an interface, this reaction will be influenced by the characteristics of this interface, such as the potential difference that is established in equilibrium and changes in potential across the interface in function of distance.

The potential of the electrolysis is strongly dependent on current density, effluent conductivity, distance between the electrodes and the surface condition of the electrodes.

1.3.1. Parameters influencing electrolytic processes

1.3.1.1. pH

The EC process performance is greatly influenced by the pH of the solution [46]. Considering only mononuclear speciation, the total aluminum present in solution (α) at a given pH value can be calculated (Figure 2). This distribution diagram shows the extent of hydrolysis, which depends on the total metal concentration and pH. As the pH increases, the dominant species changes, in this case from the Al^{3+} cation to the $Al(OH)_4^-$ ion not participate in the coagulation reactions and tend to remain in solution [47].

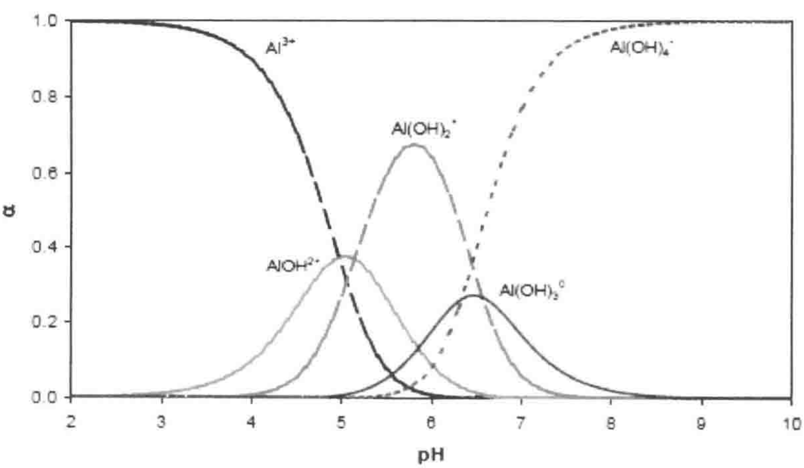

Figure 2. Diagram of distribution for Al-H_2O considering only mononuclear species (Source: [25]).