

## Scaling Prevention in the Wet Processing of Calcitic and Dolomitic Phosphate Rock.

S Chouai<sup>a\*</sup>, and PA Young<sup>b</sup>

<sup>a</sup>University of Oum El Bouaghi, Algeria.

<sup>b</sup>Head of Department of Mining and Mineral Sciences, University of Leeds, United Kingdom.

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#### \*For Correspondence

University of Oum El Bouaghi,  
Algeria.

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#### ABSTRACT

The aim of the present study is to investigate the possibility of scale prevention in the wet processing of calcitic and dolomitic phosphate rock. The mechanism of scaling is known in many field of engineering by the name fouling. The term fouling, originally a descriptive expression used in the oil industry, became established in the literature to mean any undesirable deposit on heat exchange surfaces which increases resistance to heat transmission. Such deposit is the set down of matter originally present in the fluid on the wall of flow channels. The work described in this study is confined to calcium carbonate scaling and the prevention of scaling from a suspension of phosphate rock.

#### INTRODUCTION

Calcium carbonate is the main scale species in the treatment of phosphate rock in the industry. The problem of scaling has already caused many losses in the plant of the treatment of phosphate rock in Algeria. The problem starts at the beginning of the treatment line. After crushing and grinding, the phosphate is mixed with water to form a pulp. In this stage most of the clay is eliminated from the product. This operation is carried out in a tank having two antagonist movements. After a certain period of working, the tank became fouled of calcite scaling, which is hardly removed. The second place which has the same problem is the washing plant, where all pipelines and tanks are fouled with calcite deposition.

#### Mechanism of scaling

Fouling is not only a problem in heat transfer surfaces, but is a problem in all the industry involving heat and mass transfer, like oil refinery, distillation plants, desalination plants, in the power generation industry and in the minerals industry where the most and delicate problem of scale deposition, causes many losses in production and in equipment.

Depending on the fouling mechanism, the deposition rate can be formulated in a number of ways. One of the most common causes of fouling is the crystallization of an inverse solubility salt as it described by Taborek [4], as it is shown in figure 1. These curves exhibit decreasing solubility with increasing temperature, resulting in the formation of deposit especially on heated surfaces.

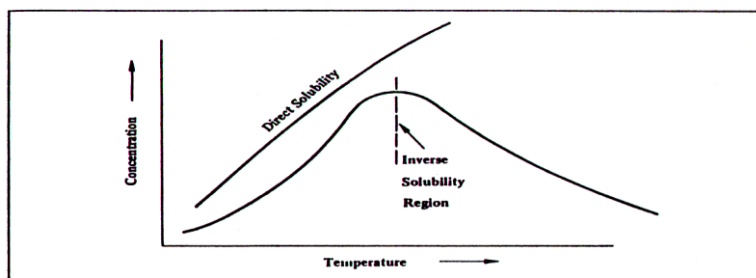


Fig.(1) The mechanism involved in the crystallization of inverse solubility salts

## Classification of Fouling

Fouling can assume several quite different basic forms, as well as being effected by a number of operational and equipment construction variables. The various fouling types and the associated interacting parameters are governed by specific sets of physic-chemical relations and will react differently to operating conditions and require separate analysis for predictive methods. The classification system has been rationalized and a generally accepted scheme is that put forward by Epstein <sup>[2]</sup>, in which the fouling categories are descriptive of the dominant fouling processes.

The fouling processes and factors affecting them can be grouped as follows:

- Fouling by sedimentation,
- Fouling by chemical reaction,
- Fouling by coking,
- Fouling by biological growth,

## Variables of Fouling

In the fouling processes many other factors can have their effects, with respect to types, mechanisms and characteristic behavior. Taborek [1] reported that where the existing data show that a fouling resistance intervenes into the heat transfer design equations, it implies an important economic factor involving the interaction of initial equipment cost, operating cost and periodic maintenance (cleaning) cost. The following parameters seem to have the most important effect.

- Flow velocity,
- Surface temperature,
- Fluid bulk temperature

## Effect of surface material and structure

According to Taborek <sup>[1]</sup>, the types of surface and materials have a great effect on fouling rate resulting in:

- Material: possible catalytic action and corrosion
- Surface: roughness, size and density of cavities will affect crystalline nucleation sedimentation and adherence tendency of deposits.

Surface, material and structure have their greatest effect in fouling initiation rather for the continued fouling process.

Early models of removal considered that particles at the surface were subject to fluid shear forces, which are capable of removing deposits from regions bounded by weakness planes. Kern and Seaton, <sup>[3]</sup> described a model where the probability of finding such planes of weakness increases with increasing deposit thickness.

Dawson, <sup>[4]</sup>, described the phenomenon of scaling of calcium carbonate from water dependent upon the temperature and concentration of foreign ions ( $\text{Cl}^-$ ,  $\text{Mg}^{++}$ ,  $\text{SO}_4^-$ ). The nucleation in the bulk solution starts when super saturation reaches a higher level, than on a heated surface.

## Theoretical Consideration of Scaling

To most people the phenomenon of local change phase when a superheated, super cooled or supersaturated liquid is brought into contact with a solid surface is a familiar occurrence. This phenomenon is less understood in relation to the influence of the water chemistry and the microstructure of the surface. Chandler <sup>[5]</sup>, described this subject as one of great industrial importance, particularly when the surface itself causes the local superheating, super cooling or super saturation, as happens with all heat transfer surfaces, which boil, condense, freeze or crystallize a fluid. At this stage, this change of phase is a major trouble and it is more suitable if it takes places in the bulk of the fluid than at the surface. Our work is limited to the study of the formation of a solid crystalline phase in contact with a supersaturated solution ( $\text{CaCO}_3$ ) at equilibrium with a suspension of phosphate rock on a heated surface.

## Calcium Carbonate Precipitation

The precipitation of a salt can occur only if the solution is supersaturated. Such a state can be obtained by evaporation which results in a concentration change. Alternatively as the solubility of salts is temperature and

pressure dependent, the super saturation can occur due to a change in one or both of these variables. The solubility of most of the alkali carbonates and sulfates of metals decreases with increasing temperature, such as calcium carbonate ( $\text{CaCO}_3$ ), magnesium carbonate ( $\text{MgCO}_3$ ) and calcium sulfate ( $\text{CaSO}_4$ ). The present work is dealing mainly with the precipitation of calcium carbonate.

### Solubility of Calcium Carbonate

The solubility of calcium carbonate in water depends upon the presence of  $\text{CO}_2$ , whose concentration is a function of temperature and pressure of  $\text{CO}_2$  at equilibrium with water. Troup et al [6] described the temperature solubility relationship of calcium carbonate in water as shown in figure 2 [7].

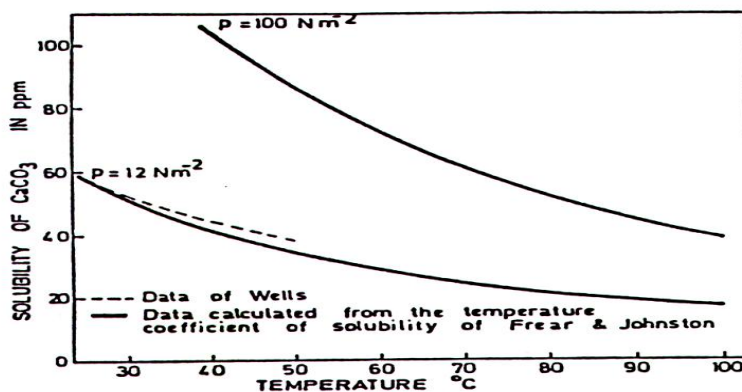


Fig.(2) Variation with temperature of calcium carbonate solubility in water

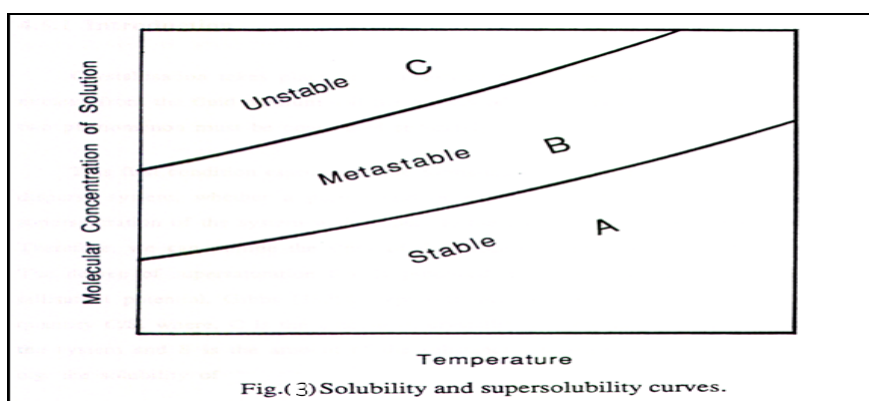
In the case of calcium carbonate, chemical reaction has a strong influence on scaling in addition to the effect of inverse solubility.

### Crystal Nucleation and Kinetic

Crystallization takes place in two distinct stages, the formation of the crystal nucleus from the fluid medium and the growth of the nucleus in that medium.

The first essential condition to the formation of a crystal from any molecularly disperse system, whether a pure liquid or vapor or a saturated solution, is the super saturation of the system with respect to the component subjected to crystallization.

Crystallization cannot occur spontaneously until a sufficient degree of super saturation has been attained able to overcome the tendency of the smallest aggregates to disintegrate into molecules. Such crystallization may be shown as a super solubility curve, as in the following figure 3.



### Crystal Growth

As soon as a stable nuclei has been formed in supersaturated solution, either homogeneously or heterogeneously, the crystal begins the stage of growth. Gibbs, [8] described the mechanism of crystal growth as primarily dependent upon the super saturation degree of the solution. The processes involved in the mechanism of crystal growth are classified under three general headings are:

- *Theories of Surface Energy*

The surface energy theories are based on the postulation of Gibbs [8] stating that the shape a growing crystal is supposed to have a minimum surface energy, also suggested that the growth of crystal could be considered as a special case of this principle.

- *Theories of Diffusion*

The diffusion theories originated by Noyes and Whitney [9], and Nernst [10], presume that matter is deposited continuously on a crystal face at a rate proportional to the difference in concentration between the point of deposit and the bulk of the solution.

Nernst [10] suggested that there is a laminar film of liquid adjacent to the growing crystal face, through which molecules of the solute would diffuse.

Berthoud [11] suggested a theory of diffusion of crystal growth, where there were two steps in the mass deposition: a diffusion process, by which a molecules are transported from the bulk of the fluid phase to the solid surface, followed by a first order reaction when the molecules arrange themselves into the crystal lattice.

- *Theories of Adsorption-layer*

The concept of a mechanism of crystal growth is based on the existence of an adsorbed layer of solute atoms or molecules on a crystal face.

### Development of the Apparatus (rig)

An experimental rig to study scaling, was initially conceived by Prof. P.A. Young, and Mr. A. Hanusch, [12] formerly head of the department of Mining and Minerals Engineering, University of Leeds, to examine the possibility of precipitation of calcium carbonate from an aqueous suspension of phosphate rock. Therefore, we started with a simple rig to carry out the experiment until at the end we designed a test rig in which we can control most of the variables which are thought to effect scaling, such as temperature, flow velocity, surface and particle size, and to some degree the pH.

Scaling caused a great problem in many different factories, and one of these is the factory of phosphate in Algeria (Djebel-Onk). The factory is in a very difficult situation. The loss in the quality of the final product is becoming more and more serious, due to poor treatment where all the equipments, e.g. tanks, and pipelines are working in half efficiency, owing to scale deposit.

### Preparation of the Suspension

After crushing and grinding of phosphate rock, the product is ready for calcinations in a laboratory electric furnace at about 960 to 965 °C during one hour. After cooling of the product it is mixed with natural water (tap water) at a ratio 1:3 (v:v), and then the suspension is placed in the rig.

### EXPERIMENTAL RESULTS

The principle of this experiment is to determine the effect of temperature on scale formation.

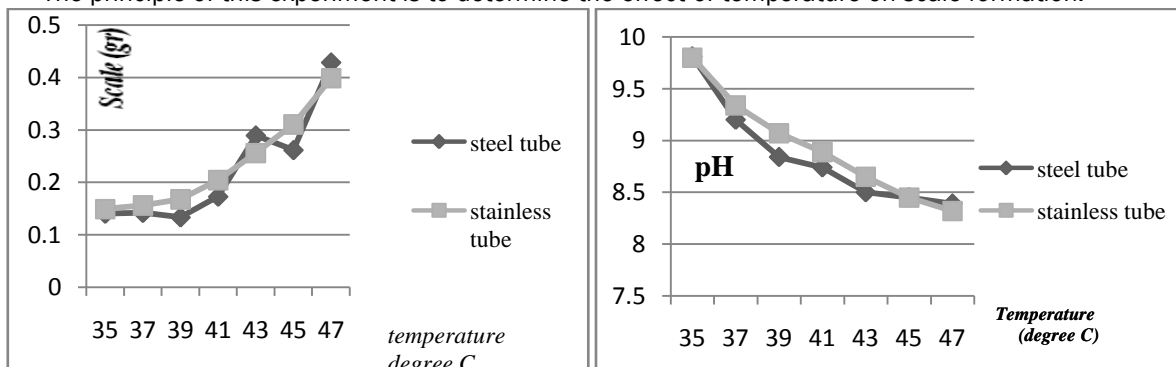


Figure 4: Effect of temperature on scale(experiment with feed 1)

Figure 5: Effect of temperature on pH (experiment with feed 1)

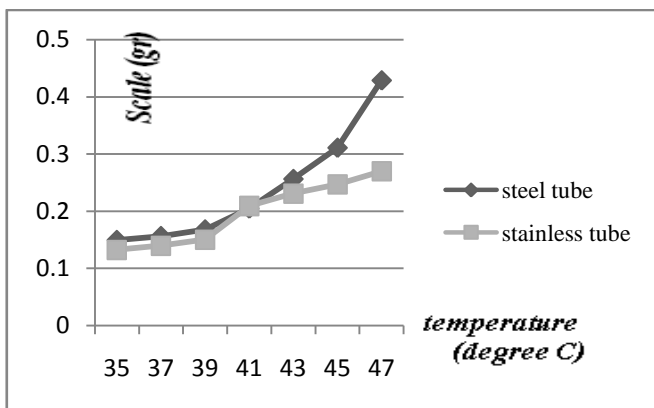


Figure 6: Effect of temperature on scale (experiment with feed 2)

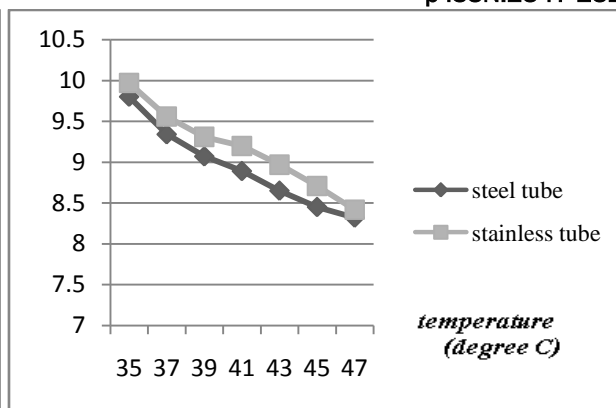


Figure 7: Effect of temperature on pH (experiment with feed 2)

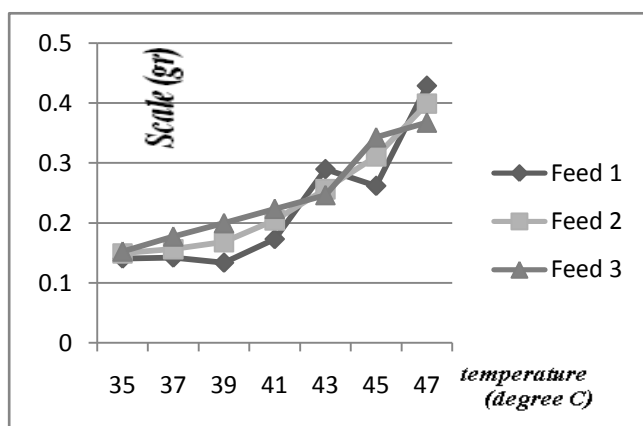


Figure 8: Effect of temperature on scale experiment with mild steel tube

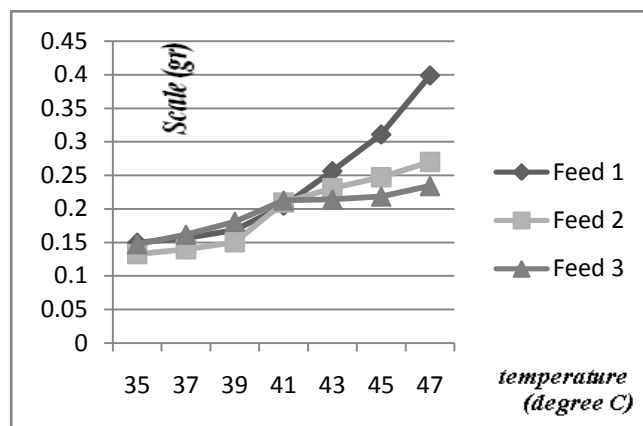


Figure 9: Effect of temperature on scale experiment with mild steel tube

### First Conclusion

After these experiments one can say that the surface of the mild steel tube is corroded and it is very hard to remove the deposit. For the stainless steel tube the opposite case takes place: the surface is clean and it is easy to take off the deposit. The difference in the properties is evident, in terms of the weight and color of the scale. The weight of the deposit from the mild steel tube is statistically greater than the deposit taken from the stainless steel tube. The color of the deposit from the mild steel tube is red, but for the deposit from the stainless steel tube is grey. Therefore, the surface of the exchanger has a great effect on scaling deposition. In economic point of view, the work carried out aims mainly at finding a solution to the scaling problem on the surface of mild steel tube as used in practical installation.

### Scale Prevention

Numerous methods for the prevention of scale especially in distillation processes are known, but are quite expensive. The choice of the correct method depends critically on:

- The nature of the raw materials or water,
- The operating conditions of the process,

Scale prevention methods can be grouped into several classes:

- Design of the unit and process so that scale has no possibility to form,
- Removal of scale-forming salts before distillation,
- Addition of compounds that delay scale deposition,
- Addition of chemicals,
- Precipitation of the scale in special easily cleanable towers.

The most important factor in scale prevention is the choice of the lowest possible operating temperature, since super saturation increases with the temperature. Unfortunately this operation method usually requires large equipments. It is necessary to strike the correct economic balance between scale reduction and operating cost, on one hand and low capital investment on the other. These factors also depend on the design of the unit and the process operating conditions [13].

To reduce the effect of scale deposition in the process of treatment of phosphate rock we tried several methods. We have introduced device in the rig of experiment, and also we have added chemicals reagent or inhibitors to the suspension.

### Experiment with Device

The device used in this experiment is called Colloid-A-Tron or (CAT. The results of the experiment are displayed below.

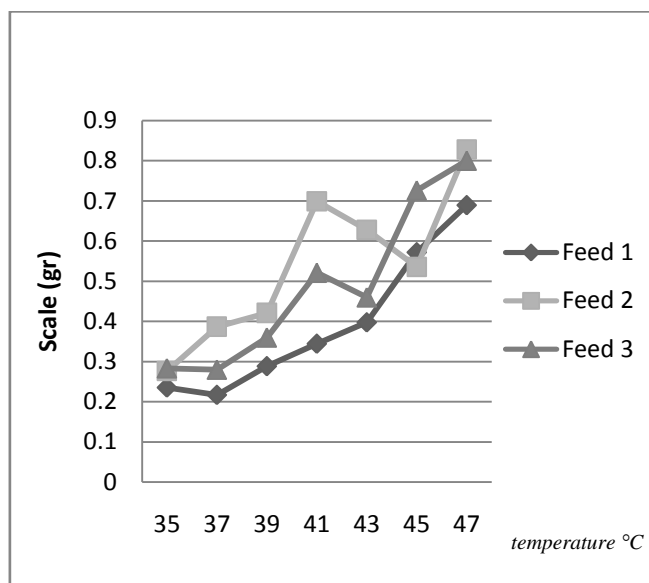


Figure 10: Effect of CAT on Scaling with variation of temperature

### CONCLUSION

After three consecutive experiments with different feed, we have obtained the result which was greater than the rate of scale obtained in the experiment without a device or inhibitor.

### Scale with the Presence of Inhibitor

The other method used to prevent scale deposition is the addition of inhibitor or chemical reagent to the solution or suspension. The addition of inhibitor is applied to many fields of water treatment and in the oil industry. In this work we try to apply this method to prevent a scale nucleation or to prevent the growth of nuclei in the suspension of phosphate rock.

These anti-scaling are commonly polyacrylate type products. These chemicals reagents were supplied to us by the Allied Colloids Company, and under proper conditions.

These anti-scaling supplied by Allied Colloids Company are in to different groups, which are

- Group 1- Acid forms,
- Group 2- Copolymers with polyacrylate

In a group 1 we have two types of inhibitors, which are

- Antiprex A
- Antiprex 461

And in the second group also we have two types of inhibitors, which are

- DP9 2160
- DP9 2162

The chemical reagent received from the company is 40 % active for the group of copolymers with polyacrylate, and for the group of acid forma is 45 % active, but for the use of such inhibitor it is recommended that it should be at 1 % active, secondly it must be a fresh solution for each day or for each run.

Results of the experiment are displayed in the following figures

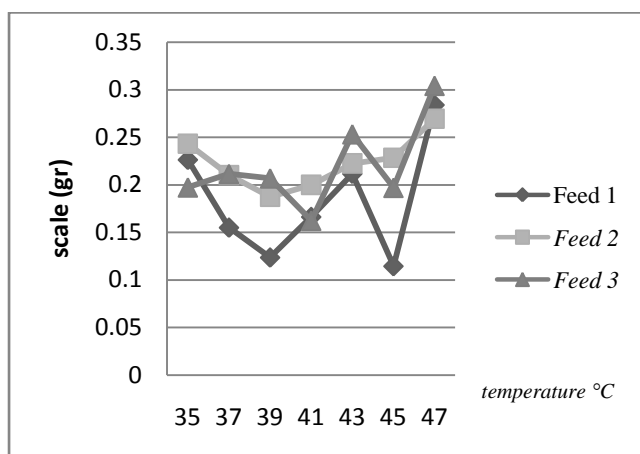


Figure 11: effect of temperature on scaling with the inhibitor Antiprex A

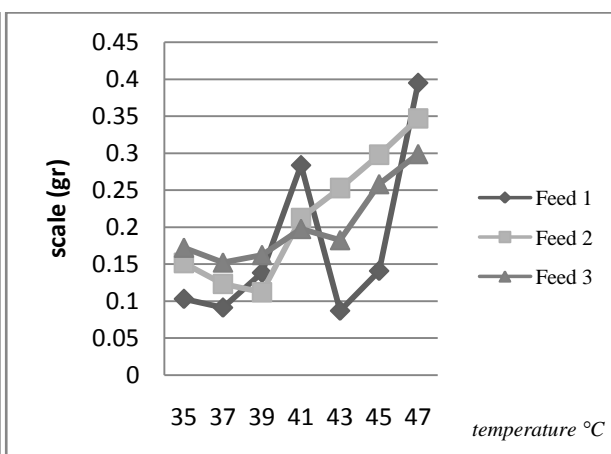


Figure 12: effect of temperature on scaling with the inhibitor DP9 2162

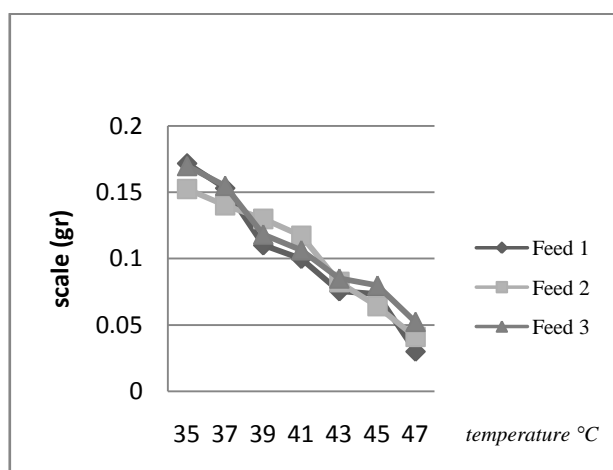


Figure 13: effect of temperature on scaling with the inhibitor Antiprex 461

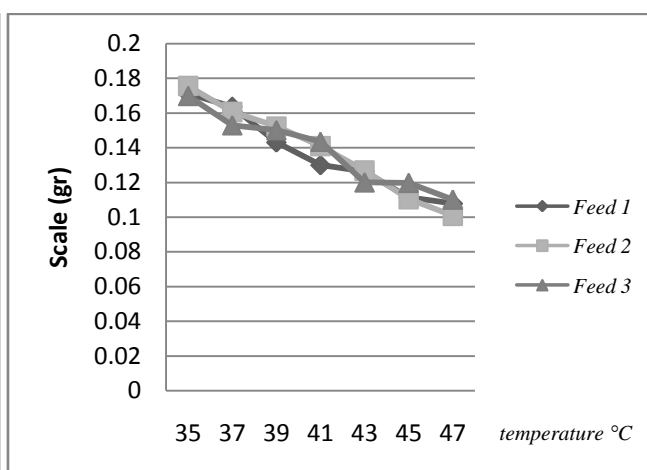


Figure 14: effect of temperature on scaling with the inhibitor DP92162

After these experiments with the presence of inhibitors at the dosage of 20 ppm, we have found the best result is with the chemical reagent Antiprex 461, than we have carried out the experiment with the inhibitors but at different dosage for each reagent form 5 ppm until 50ppm. Also in these experiments the best results is with the Antiprex 461.

Here are shown the effect of inhibitor Antiprex 461 with different dosages.

This study describes an investigation into the mechanisms of scaling and scaling prevention in the wet processing of calcitic and dolomitic phosphate rock. Scale has already caused so many losses in the factory of treatment of phosphate rock at *Djebel-Onk* (Algeria).

Scale is a deposit of minerals which forms on solid surfaces of industrial equipment. The presence of scale leads invariably to operating difficulties and/or loss of efficiency.

The composition of scale depends on the raw material or water composition and operating conditions. Scale usually contains the following chemical compounds; magnesium oxide, calcium carbonate, and calcium sulfate. The formation of scale can occur where the solubility limits of these compounds are exceeded.

After several experiments we have found the weight of scale increases with increase in temperature, the weight of scale was between (0.14 - 0.4gm). The weight of scale taken from a mild steel tube was greater than the weight of the scale taken from a stainless steel tube. The surface of the tube (mild steel tube) was completely

covered with corrosion, and it was very clear on the color of the deposit. The deposit taken from mild steel tube was red, and the one from stainless steel tube was grey.

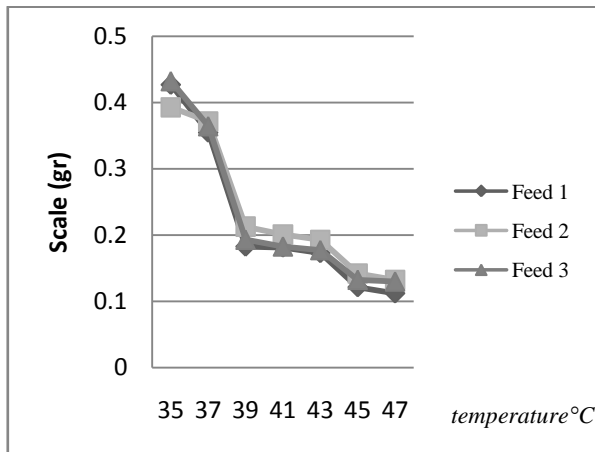


Figure 15: effect of temperature on scaling with the inhibitor Antripex 461 (10 ppm)

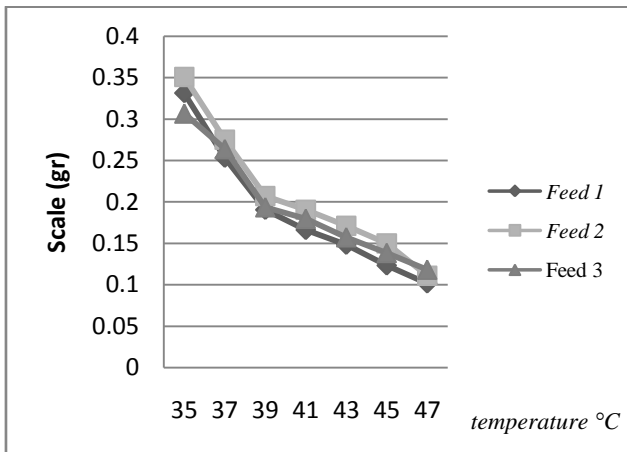


Figure 16: effect of temperature on scaling with the inhibitor Antripex 461 (15 ppm)

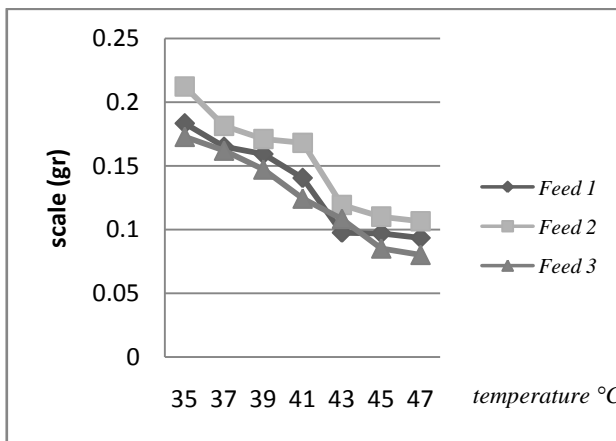


Figure 17: effect of temperature on scaling with the inhibitor Antripex 461 (30 ppm)

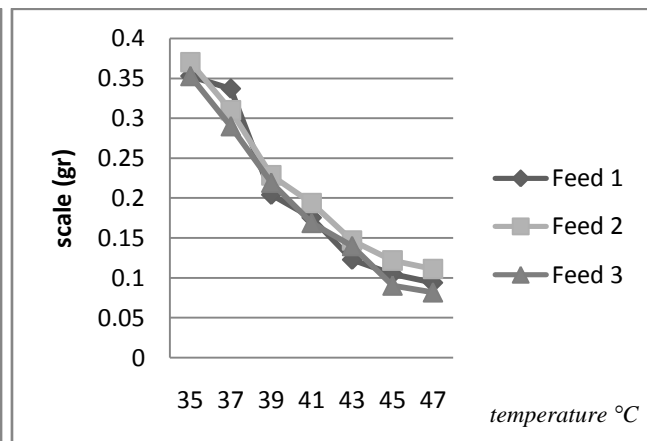


Figure 18: effect of temperature on scaling with the inhibitor Antripex 461 (40 ppm)

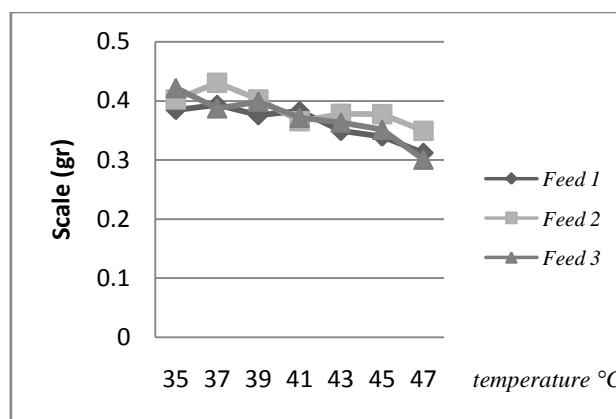


Figure 19: effect of temperature on scaling with the inhibitor Antripex 461 (50 ppm)

Finally, we have looked at two different methods to solve the problem or to decrease his effect on the industry.

The first method was the installation of device called Colloid-A-Tron (CAT), before the test section in the rig, and the other entire factor are kept constant.



The weight of scale in run was over range of 0.23 – 0.8 gm, and the surface of the tube was absolutely corroded.

The second method employed in this investigation was the addition of chemicals reagents. In this work we have used two types of chemicals, which are acid forms, and copolymers with polyacrylate.

In the first group we have two reagents; ANTIPREX A, and ANTIPREX 461. In the second group we have DP9 2160, and DP9 2162.

In the beginning we have determined which of these inhibitors has the most effect on scale deposition, then we taken the reagents ANTIPREX 461, and DP9 2160 because their effect was considerably efficient than the others. However, we started to determine the optimum dosage for the prevention of scaling. The dosage of the two reagents was over a range of 10 – 50 ppm.

After the addition of antiscalants to the suspension there was an effect on scale deposition, the weight of scale deposition was decreased, and the surface of the tube become clean. The operation to take off the deposit from the tube becomes also easy.

The optimum dosage in this work for the reagent ANTIPREX 461 was 20 ppm, and for the reagent DP9 2160 was 10 ppm.

The mechanism of preventing scale nucleation and/or crystal growth has been reached in this investigation by the addition of antiscalants.

The inhibiting action has been interpreted in terms of the adsorption of the additive molecules on the growing agglomerate (nuclei) preventing further growth and thereby promoting its net dissolution.

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