An Interesting Final-Year Undergraduate Laboratory Project: Investigation of Gypsum Scale Formation on Piping Surfaces

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The formation of scales in pipes and on the surfaces of vessels is one of the major problems encountered by the mineral processing industry in Australia and elsewhere. A cursory study revealed that one of the main components of the scales was gypsum or calcium sulfate dihydrate. This paper discusses a typical undergraduate laboratory project to investigate the formation of calcium sulfate dihydrate scale on the surfaces of different types of pipes under isothermal conditions. This laboratory exercise is essentially a crystallization process and is suggested as one of the topics for final-year chemical engineering undergraduate project since it is a very important unit operation in the chemical, mineral, or pharmaceutical industries.

Keywords: Calcium sulfate dihydrate, laboratory project, scale formation, *and* undergraduate curriculum.

INTRODUCTION

In most modern-day chemical engineering curriculum, a laboratory project is usually essential for accreditation purposes. As a project usually takes about one semester to complete, it gives a student an opportunity to explore in-depth a certain topic of his or her interest. A laboratory work can have as many as ten goals beneficial to students (Wankat and Oreovicz 1993). It develops experimental skills and through oral and written reports communication skills are also enhanced. It serves to illustrate to students the nature of open-ended problems with no single solution which is commonly encountered in class assignments (Miller et al. 1998).

The Department of Chemical Engineering at Curtin University of Technology has been and is greatly involved in assisting the mineral processing industry to alleviate the burden of scaling in practice. In addition, at the Department of Chemical Engineering, crystallization is taught as one of the topics in the final year undergraduate curriculum. Since the formation of scales (*scaling*) is essentially a crystallization process, a laboratory project involving crystallization can be developed as an investigation on scaling.

Later discussion in this paper will show that this particular laboratory project is versatile so that frequent and expensive updating of laboratory equipment can be avoided. This paper attempts to show how a laboratory-based final project

could be conducted. Calcium sulfate dihydrate scale formation was taken as a typical example. All the necessary steps for the implementation of the laboratory project were elaborated.

STRUCTURE OF THE LABORATORY PROJECT

The project is divided into three major stages spread over a semester that lasts about 14 weeks.

Stage 1. Literature Survey and Experimental Design (three weeks)

The student is given a broad guideline on the topic to explore. Some guidance in setting up the experiment are also given. The details are not spelled out to give a student the opportunity to develop his or her own ideas. For example, a student is told about the effects of additives on scale formation, but not of the concentration ranges or temperatures the additives must be used.

The objective is to encourage the student to do literature search and to come up with an appropriate proposal. Furthermore, the student may need to consult practitioners in the mineral processing industry as to what types of additives are of interest to them. At this stage, a *deliverable*, in the form of a literature review or an experimental design, will be required in order to guide the laboratory work in detail.

Stage 2. Laboratory Work (nine weeks)

The laboratory work includes trial runs to check the applicability of the variables, which have been set out in the experimental design. At this stage, apart from interaction with the supervisor, the student may have to consult laboratory technicians as resource persons.

Again, a deliverable is required at this stage, now in the form of brief written reports, which should be handed in every second or third week. This requirement allows early feedback for the work, especially when something needs to be rectified.

Stage 3: Data Analysis, Report Writing, and Oral Presentation (two weeks)

The student needs to: analyze the experimental data obtained, document the laboratory work, submit the report, and make an oral or poster presentation of the findings.

CALCIUM SULFATE DIHYDRATE OR GYPSUM SCALE-FORMATION AS A CASE STUDY

Scaling, or *crystallization fouling*, is the phenomenon of deposition of a hard crystalline layer on a heat transfer surface. It is primarily caused by dissolved inorganic components crystallizing out of the solution, which is supersaturated with the dissolved components.

Scaling is a persistent problem in many industrial processes. Desalination installations, cooling water systems, chemical processes involving evaporation and/or crystallization, potable water supply lines, and mineral processing plants are examples where severe scaling problems are usually encountered.

Scaling in pipes and on surfaces of vessels causes serious operational problems as well as increasing costs of pumping and replacement of parts. A cursory study revealed that one of the main components of the scale deposit in some industries was gypsum or calcium sulfate dihydrate crystals (Northwood 1995). It is immediately apparent, therefore, that a better understanding of the behavior of calcium sulfate dihydrate scaling is necessary.

With supersaturation level as the key factor, the scaling phenomenon is not confied to heat transfer surfaces. It also occurs under isothermal conditions or at ambient temperatures. One such condition is the scaling problem in potable water supply systems, where the pipe lines that carry the water do not undergo appreciable changes in temperature.

Mechanism of scaling

The review on precipitation fouling or scaling given by Hasson (1981) is probably one of the most comprehensive. The review describes the

general mechanism of scaling once the supersaturated condition is established. The mechanism proceeds through five steps as explained below. However, there is no clear cut limit to each step.

Step 1. Nucleation

Nucleation is the formation of nuclei or active centers. The nuclei attach to the solid surface or, in the case of a higher supersaturation level, to the bulk of the solution. The nuclei subsequently grow to become crystals.

Step 2. Diffusion

Diffusion is the transport of scale-building components, such as ionic species, solvated ions, molecules, and particulate solids, to the solid surface. In a pipe or tubular unit, it is customary to assume that scale components move radially to the wall of the pipe.

Step 3. Deposition

The transported materials will eventually reach the scale-liquid interface and adsorb onto either the crystal surface or the solid surface. In some cases, surface reaction may happen. The result of the deposition step is the growth of the attached crystals, which is essentially the growth of the scale layer.

Step 4. Removal

If the scaling solution is not stagnant, the depositing layer will experience shear stress induced by the flowing fluid. This stress may cause the layer to detach from the solid surface and be swept away by the fluid. Depending on the strength of the deposit layer's attachment to a surface, the removal step can be a significant factor in scale formation. The removal and the deposition steps may occur concurrently and dictate the extent of a layer's scale deposit.

Step 5. Aging

Aging of the scale deposit is obviously a time-dependent process. It is argued that aging strengthens the deposit layer through a number of crystal modifications. On the one hand, changes to the scale, such as recrystallization, phase transformation, and Ostwald ripening, are believed to strengthen scale deposits (Cowan and

Weintritt 1976, Andritsos and Karabelas 1992). On the other hand, changes in temperatures, which are common to heat transfer surfaces, produce thermal stress that causes the deposit to flaking off. The aging phenomenon can be complicated further by differences in the structure of the deposit, such as in density and porosity, causing different responses to thermal stress (Andritsos and Karabelas 1992, Sheikholeslami 2000).

The five steps in the scaling mechanism may occur concurrently or consecutively. In addition, any two mechanisms may produce a synergistic effect (Hasson et al. 1996).

Scaling under isothermal conditions

Some scale formation take place without a temperature gradient. In potable water supply lines, for example, the deposition of scales usually occurs at ambient temperatures. Scale deposition on pipe surfaces in mineral processing plants, such as in copper/zinc concentrate production, also occurs under comparatively isothermal conditions. In this particular type of plant, the scale forms throughout the flotation water piping system without appreciable heat transfer (Northwood 1995).

The scale formation study presented in this paper was carried out at ambient temperature to simulate the condition in a flotation piping system in a mineral processing plant.

EXPERIMENTAL

A number of factors are operative and, thus, influence the mechanism of calcium sulfate dihydrate scale formation. Since the formation is essentially a crystallization phenomenon, there is no doubt that the supersaturation level of the crystallizing solution is the dominant factor. Therefore, the first factor investigated in this study was the supersaturation level. The other factors that were studied were also discussed.

1. Supersaturation level

Preliminary trials showed that at supersaturation levels below 2,000 ppm with respect to Ca^{2+} the

amount of scale formed on the surfaces of the coupons (explained in the section on *Description of the experimental set-up*) was too small that the accurate weighing of the scale became extremely difficult. Likewise, the removal of the scale without damaging the scale structure from the coupons for subsequent scanning electron microscopy (SEM) examination proved difficult. In contrast, using supersaturation levels above 6,000 ppm Ca^{2+} resulted in very rapid scale deposition and clogging of the test section. (See section on *Description of the experimental set-up* for test section description.) It was, thus, decided that the experiments be conducted at supersaturation levels between 2,000 and 6,000 ppm of Ca^{2+}.

2. Flow rate of solutions

Low flow rate values (0.4–1.3 cm/sec) that correspond to the Reynolds number in the laminar region were chosen to make the effect of the removal phenomenon on scale deposition negligible. Moreover, with the low flow rate, the volume of the solutions to be prepared was minimized and the handling of the experiment was made easier.

3. Type and concentration of impurities

Sodium isopropyl xanthate (SIPX), a biodegradable flotation agent commonly used in the mineral processing industry, was chosen as for this project.

4. Type of piping materials

It is well known that process equipment use different types of materials depending on the chemicals or substances that they process. The same situation applies for piping systems. In this laboratory project, the effects on four types of piping materials—PVC, copper, brass, and stainless steel—were studied.

Description of the experimental set-up

The experimental set-up used in this laboratory project is illustrated in Figure 1. It consists of two major parts: (a) two vessels, each with a working volume of up to eight liters, where the scale-forming solutions were kept; and (b) a test section where the scale formation was expected to occur. One of the vessels contained $CaCl_2$ solution as Ca^{2+} provider, while the other vessel contained Na_2SO_4 solution as SO_4^{2-} provider.

The two solutions were transported through the test section using a peristaltic pump (Masterflex™ peristaltic pump supplied by Cole Palmer Instrument Co.) at predetermined flow rates. The peristaltic pump was fitted with two heads to ensure consistent and accurate flow rates for the two solutions.
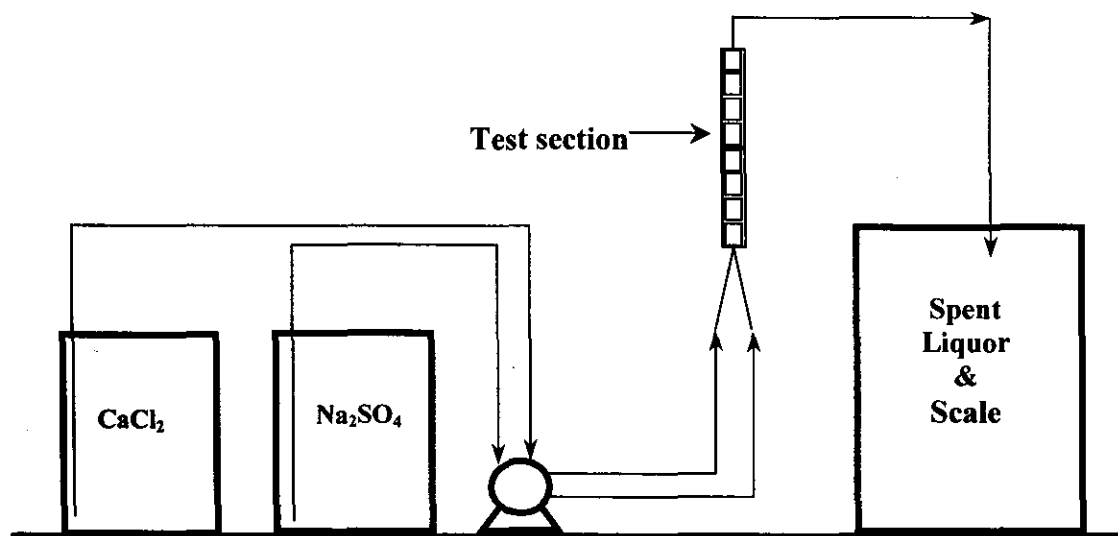

Figure 1. Schematic Representation of the Experimental Rig

To avoid possibile nucleation in the solution before the test section, the two solutions were transported separately from their respective vessels. Thus, mixing of the solutions occurred just at the inlet of the test section where the two solutions met. The test section consisted of two flanged tubular units made of stainless steel and eight pairs of semiannular coupons, which could be inserted into the tubular units to serve as scale surfaces (Andritsos and Karabelas 1991). The flanged tubular units had a length of 8 cm and an inner diameter of 1.8 cm. Each semiannular coupon had a length of 2 cm and an internal diameter of either 1.3 or 0.7 cm.

In order to firmly fix the alignment of the two tubular units, tongues and grooves were machined onto their opposing flanges. The spent liquor coming out from the test section was collected into a vessel to allow more gypsum to crystallize out of the liquor. The spent liquor and the gypsum formed were then discarded. All accessories were thoroughly cleaned with flowing tap water followed by rinsing with distilled water to avoid contamination. Prior to cleaning, a dilute HCl solution was used to soak the tubular units and the coupons after each experimental run to dissolve and remove traces of adherent scales.

The admixtures used in the experiments were dissolved in distilled water and then added into the vessel containing the Na_2SO_4 solution. The solutions entered the test section from the bottom side in order to lessen the effect of gravity, which could induce the removal of scales. In addition, to achieve a downward flow, the fluid must flow fast and fully occupy the pipe cross-section; otherwise, it will tend to flow down one side of the pipe. In such a case, parts of the pipe, which were not covered by the fluid, would stay dry, resulting in non-uniform scaling.

Preparation of the supersaturated solutions

The gypsum-forming solutions used for the experiment were prepared by making equimolar amounts of stock solutions of calcium chloride and sodium sulphate, respectively. The calcium chloride solution was made by dissolving $CaCl_2 \cdot 2H_2O$ crystals in distilled water at room temperature followed by filtration through

0.22 μm Millipore™ filter paper (Amjad 1985). The sodium sulphate solution was prepared in the same manner. The two solutions were kept separately and extreme care was taken to keep the solutions free from dust and insoluble matter.

Preparation of the test section

Before each experimental run, both the tubular units and the semiannular coupons were washed with detergent and flowing tap water followed by HCl soaking and rinsing with acetone and distilled water. Subsequently, the coupons were dried in an oven, allowed to cool, and carefully weighed. Then, they were inserted into the tubular units. Finally, the tubular units with the semiannular coupons inside were fitted onto the experimental rig.
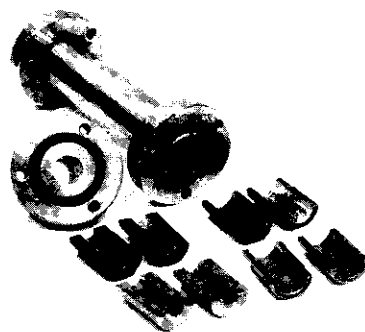
Figure 2. The Test Section: The Coupons, the Tubular Unit, and the Flange

Description of a typical experimental run

As described previously, a predetermined amount of calcium chloride and sodium sulphate solutions were placed in separate vessels to provide a certain supersaturated gypsum solution for the test section. For the experimental runs using admixtures, the admixture solution was added into the Na_2SO_4 solution. The pump was activated and the starting time was recorded. Occasionally, all the connecting tubes were checked for flow rate and leakage and to ensure that no air bubbles formed inside the tubes. Otherwise, the bubbles would interfere with the flow rate uniformity and/ or the deposition mechanism. At the end of the run, the pump was switched off. The tubular test section was disconnected and left in a vertical position until no more drippings of the solution

were seen. The semiannular coupons were carefully withdrawn from the tubular units and were placed overnight in an oven at a temperature of 100°C. The following day, the coupons together with the adherent scale were weighed. The difference between the weight before and after the experiment is the weight of the mass of the scale deposit. The scale samples obtained were morphologically analyzed using SEM (Phillips XL30).

RESULTS AND DISCUSSION

It is evident that each step in the experimental runs is subject both to random errors and systematic errors. Random errors will very likely occur in the following steps:

1. Weighing and dissolving crystals of both $CaCl_2 \cdot 2H_2O$ and Na_2SO_4 for the scale-forming solutions,
2. Subsequent measuring of the volumes of the scale-forming solutions,
3. Reaction time in starting and stopping the peristaltic pump,
4. Reaction time in starting and stopping the stopwatch to time the experimental run, and
5. Weighing the mass of the scale deposit.

Likewise, all the equipment used in the above steps—including balances, volumetric flasks, peristaltic pump, and stopwatch—would be subject to systematic errors. For example, if the pump was run consistently slow, then all the experimental flow rates would be underestimated and vice versa.

In most teaching laboratories, the systematic uncertainties of all equipment used, in the absence of more specific information, have usually been identified and established (Taylor 1997). As an example, a volumetric flask of two-liter capacity may have a systematic error or uncertainty of ±0.6 ml at 20°C.

In this laboratory project, however, the uncertainty of the two-liter volumetric flask had been pegged at ±0.6 ml regardless of temperature. This was considered satisfactory since all the experimental runs were conducted at room temperature of ±20°C. Similarly, it might be decided that all balances had up to one percent

uncertainty (Taylor 1997). Briefly, all of the equipment used in this scale-formation laboratory project had been considered to have some known definite uncertainty that contributed to the systematic error. Thus, in the error analysis, both random errors and systematic errors should be taken into account.

The general formula proposed by Taylor (1997) for error propagation was used for error analysis with the assumption that all errors were independent and occurred at random. The formula showed how the uncertainties in a certain step propagated through the calculation such that the final results effectively included an accumulation of the said error propagation.

In all the graphs presented in this paper, the weight of the scale deposit (= vertical axis) was shown with error bars, since it was evident that the final product was subject to more appreciable uncertainties than all the corresponding components along the horizontal axis.

Effect of supersaturation
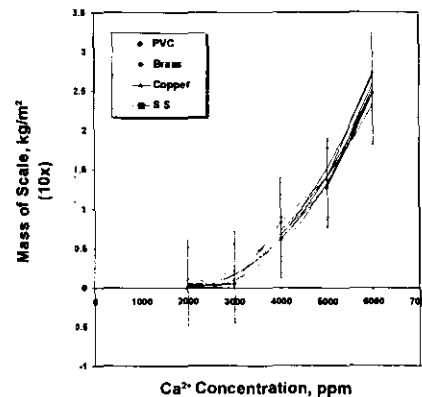
Figure 2. Effect of Supersaturation Level on Scale Deposition for Various Piping Materials

Since supersaturation is the primary driving force in crystallization and, therefore, in the scale formation, an increase in supersaturation level is expected to result in more calcium sulfate dihydrate scale deposits on the pipe wall. Figure 3 illustrates this situation. In all experiments using different types of piping materials, the mass of deposited scale increases with increasing supersaturation levels.

It is interesting to know at what supersaturation level the scale starts to deposit on the pipe surface. This is determined by drawing regression lines for each of the pipes as shown in the figure.

Table 1. Regression Correlation Between Type of Pipe Materials and Mass of Scale Deposited

Pipe materials	Regression Equation	R^2
PVC	$Y=1.10^{-7}X^2-0.0003X+0.2550$	0.98
Brass	$Y=2.10^{-7}X^2-0.0007X+0.6986$	0.99
Copper	$Y=2.10^{-7}X^2-0.0007X+0.7748$	0.99
Stainless steel	$Y=2.10^{-7}X^2-0.0008X+0.8350$	1.00

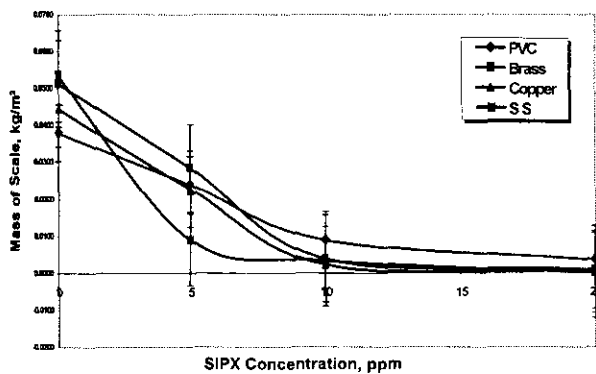**Table 2. Correlation Between Pipe Materials and Threshold Ca2+ Concentration for Scale Deposition**

Pipe Materials	Threshold Ca^{2+} Concentrations, *ppm*	R^2
PVC	1,500	0.98
Brass	1,750	0.99
Copper	1,750	0.99
Stainless steel	2,000	1.00

Figure 3. Effect of SIPX Concentrations on the Scale Deposited for Various Piping Materials (at a low flow rate of 0.4 cm/sec)
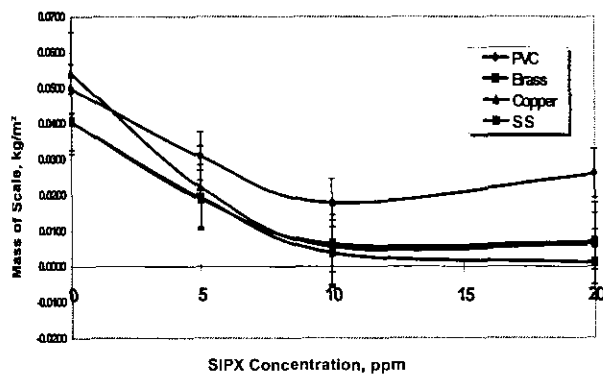
Figure 4. Effect of SIPX Concentrations on the Scale Deposited for Various Piping Materials (at a higher flow rate of 1.3 cm/sec)

Polynomial regression lines were found to be suitable for the correlation between supersaturation level and mass deposit as shown by their high R^2 values; i.e., e" 0.98 (see Table 1). Based on the regression lines obtained and depending on the type of piping materials used, the deposition of scale on the pipe surface was predicted to start at supersaturation levels between 1,500 and 2,000 ppm with respect to Ca^{2+}, as shown in Tables 1 and 2. These supersaturation levels are termed the threshold concentrations, below which no scaling is expected.

Figures 3 and 4 show the effect of additives (SIPX) concentrations and fluid flow rates on the mass of the scale deposited. As can be seen, higher concentrations of SIPX have higher retarding effect on the scale build up. The two figures imply that the mass of scale deposit was higher for higher flow rate. The explanation for this behavior is as follows. Fluid moving at high flow rate exerts stronger shear stress on the viscous diffusion layer, which covers the scale resulting in the thinning of the thickness of the layer.
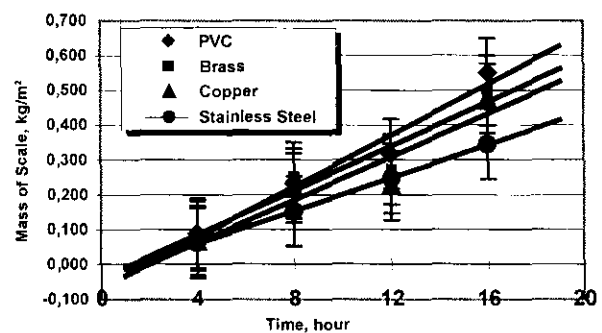
Effect of flow rate and impurity concentrations

As the layer becomes thinner the diffusion rate of the scale building components towards the wall of the pipes becomes faster. In other words, more ions or molecules or particulate matter are transported to the pipe wall. Hence, more scale will deposit. It could be argued that contact time for higher flow rate is shorter

Figure 5. Plot of Mass of Scale Deposited vs. Time for Different Types of Pipe Materials

and, as a consequence less scale materials will be deposited. Since the data obtained are contrary to this reasoning, it should be assumed that the thinning effect of the flow rate on scale deposition overrides that of the contact time.

Another possible explanation is that the newly formed scale might behave as colloidal particles, which possess surface charge (Heald and Smith 1974). Higher flow rate could have influenced the charge so that the newly formed scale was strongly stabilized. This phenomenon indicates that under the influence of SIPX as additives the scale deposition may be diffusion controlled, especially for higher concentrations. This diffusion mechanism was also observed in a full pipe flow experiment on $CaCO_3$ scaling (Andritsos and Karabelas 1992).

Effect of piping materials

Figure 5 Plot of mass of scale deposited versus time for different types of pipe materials depending on the type of materials or chemicals being processed, different types of piping materials may be used. The effect of piping materials on scaling is not well understood and it appears that the effect is mainly confined at the start of scale formation. Probably the effect is more related to the roughness of the surface, which could be different due to the type of materials as well as methods of manufacture. It is argued that once the pipe surfaces have been entirely covered by the scale layer, the roughness will have no effect on the growth of the scale. However, it may still influence the removal or the ageing process.

Microscopically, the entire surface of a pipe consists of crevices and cracks which provide sites for attachment of the scale building components when they are transferred towards the pipe wall. The characteristics of the crevices and cracks will ultimately determine the strength of the attachment. It can be assumed that the rougher the surfaces the stronger the attachment and, hence, the more difficult to detach. In another study, it was observed that the nucleation rate of calcium sulfate crystals increased with surface roughness (Linnikov 1999).

The effect of pipe materials on scale formation is determined by the amount of scale deposited on the pipe made of particular materials under otherwise the same operating conditions. In all cases, PVC was found to have the highest amount of scale deposit. This is evident from Figure 5, which shows the mass of scale deposited as a function of time. As can be seen, in most cases, PVC appears to be the most favorable site for scale formation. In descending order, the piping materials can be listed as follows: PVC, brass, copper, and stainless steel.

EVALUATION OF THE LABORATORY PROJECT

Students' response to this typical laboratory project is generally positive. They pointed out that such a laboratory project does reinforce the materials received in lectures. The students were made aware that the project is typically an open-ended type with no clear and definite results. The time spent in the laboratory, however, was often underestimated which made some students feeling either bored or under pressure towards the end of the project.

The results of the case study of calcium sulfate dihydrate scale formation presented in this paper correspond to the trend found in the plant site. A wider interaction between university and industry for the benefit of students as illustrated by this project is a win-win situation for all parties.

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