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## **THE SCALLOPING PHENOMENON AND ITS SIGNIFICANCE IN FLOW-ASSISTED-CORROSION.**

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### **ABSTRACT**

The recently observed Flow-Assisted Corrosion (FAC) of CANDU outlet feeders is associated with a texturing of the corroding surface, called "scallop", that imparts the appearance of orange peel. To study the evolution of erosion and dissolution patterns contributing to scalloping and to derive the link with corrosion, experiments on the dissolution of pipes made of plaster of Paris ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ) are being carried out.

Flow-Assisted Corrosion is a significant problem with carbon steel components handling rapidly moving water or water/steam mixtures in the power generating industry. The mechanism of FAC in outlet feeders of CANDU reactors can be described in terms of a mixture of surface dissolution and erosion controlling the thickness of the protective oxide. Erosion is influenced by the combined action of flow-induced mechanical forces (shear stresses, pressure variations by high flow velocity and particle impact in multi-phase flows) and dissolution by electrochemical processes.

The method chosen to study scalloping is the dissolution of pipes made of plaster of Paris ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ) in a recirculating water loop. The solubility of plaster of Paris in water is high enough (2.6 g/l) so that significant dissolution is obtained after a short time. The conductivity and the pH of the water flowing through the loop test section have been recorded and post-test examination has been carried out. Scallops have been observed along the plaster surface at the end of the tests. Their characteristics are strongly related to the flow rate. Scallop size decreases with increasing flow rate whereas surface density of scallops increases with increasing flow rate. It has been found that the scallop pattern develops at the upstream end of the pipe and moves downstream. The collected data are used to develop models describing the significance of scallops in FAC.

### **INTRODUCTION**

In convective transport the flow field and diffusive properties establish the distribution of the rate of mass transfer from

a surface. If the surface is soluble, an interaction between the flow and any surface irregularity can lead to the development of a rough surface that has been given the name of "scallop". This phenomenon has been

observed in many different disciplines like geomorphology and geology, astrophysics and aeronautics, and civil, mechanical and especially chemical engineering. Recently, scallops were observed in the primary coolant system of CANDU reactors (see Fig.1). It seems that the formation and the evolution of scallops in outlet feeders made of carbon steel play a major role on the thinning rate of the pipes, which is proceeding much faster than expected.

Little progress has thus far been made for understanding the size, shape and spacing of scallops and few experimental data are thus far available. Some geology workers (Allen [1], Blumberg and Curl [2,3]) have attempted to classify erosional markings and have developed theories of spacing and generalised the geometry of scallops. Two main groups emerge from these studies: one has developed what is called the "Passive-bed Theory" while the other supports the "Defect Theory" of the patterns. In fact, a good approach to describe scalping and its significance in Flow Assisted Corrosion (FAC) is to compare it with natural phenomena like erosion of mud and rocks by the sea or erosion of ice by the wind.

In order to study the evolution of this erosional pattern and to link it to the corrosion phenomenon, experiments have been made on the dissolution of plaster of Paris ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ ) in a recirculating water loop.

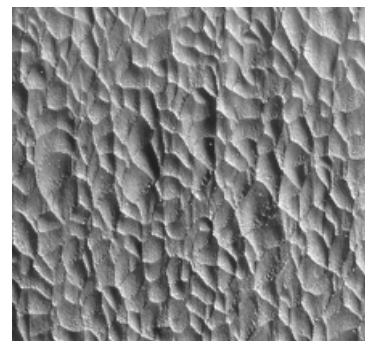
## I. THEORITICAL BACKGROUND

### Flow Assisted Corrosion

Surface scalping is symptomatic of the attack by FAC of carbon steel in boiler

feedwater systems. The main assumption in FAC is that an oxide film forms on the carbon steel surface and protects it by limiting the diffusion processes that control corrosion. If erosion and/or dissolution make the film thinner, corrosion increases. At steady state, the oxide formation at the metal surface equals its dissolution at the oxide-coolant interface. The link with coolant flow has been established: increasing the fluid velocity increases the flux of removed oxide to the bulk coolant (Lister [4]). At bends or elbows, the turbulence is very high and these places are expected to be particularly vulnerable.

The FAC in outlet feeders of a power plant can be described as a combination of dissolution-controlled and erosion-controlled corrosion. Dissolution and mass transport may act together and involve convective diffusion, while the erosion component is characterised by the combined action of flow-induced mechanical forces (shear stresses, pressure variations by high flow velocity and particle impact in multi-phase flows) and electrochemical processes.

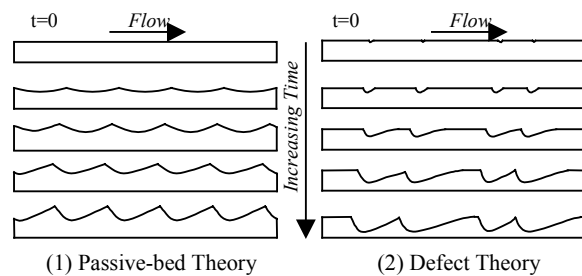


*Fig 1: Scalping on the inner surface of a carbon steel feeder pipe.*

## Geological Studies

Erosional processes have been studied in a variety of disciplines like geomorphology, geology, aeronautics and civil, mechanical and chemical engineering. The reason is that the several processes of erosion are physically analogous and often lead to similar surface markings.

Geological investigations have found the formation of erosion marks similar to those observed on the steel feeders (Lister [4]). Fig.2 illustrates the two alternative theories about the spacing, the shape and the size of scallops that came of from these studies:



*Fig 2: Evolution of a surface according to (1) Passive-bed Theory and (2) Defect Theory.*

- The *passive-bed theory* of erosional marks postulates that the characteristics of the erosion marks are entirely determined by the dynamic properties of the fluid in contact with the surface. The properties of the material have therefore no influence on the formation of the scallops. The length of the erosion marks is thus assumed constant with time. Sharp [5] and Leighly [6] proposed that the characteristics of scallops on ice surfaces were controlled by the properties of vortices in the adjacent air. Henderson & Perry [7] and Curl [4] support

the same idea with studies of meteorites and limestone caves, respectively.

- The *defect theory* postulates that the position of each erosional mark is due to the initial presence of an irregularity or a defect at the surface. It assumes an independent evolution for each mark and an increase of length and amplitude with time up to a limit set by the initial spacing of defects. Therefore, the characteristics of any assemblage of erosional marks depend on the duration of the eroding process, the spatial distribution, shape and dimensions of the defects, and the character of the flow.

## Rate of Dissolution of Plaster

The dissolution rate of a solid in an aqueous solution without any further reaction between the formed ions is controlled by:

- Chemical reaction at the surface (which depends on the chemical composition of the solution on the surface).
- Molecular diffusion through the boundary layer.

In both cases, at steady state, mass flow resulting from the dissolution of the surface,  $R_s$ , is equal to the mass flow of the transport through the boundary layer,  $R_t$ .

Two extreme cases exist:

- If the thickness,  $\epsilon$ , of the boundary layer is very small, the transport by diffusion is very effective and the surface concentration of the dissolved species is close to that in the bulk. The rate of dissolution is then controlled by the kinetics of dissolution on the surface. A general equation for the surface-controlled dissolution rate,  $R_s$ , is (Lasaga [8]):

$$R_s = k_s \left(1 - \frac{C_s}{C_{eq}}\right)^n = k_s (1 - \hat{C}_s)^n \quad (1)$$

where is  $C_s$  the total concentration of dissolved species at the surface,  $C_{eq}$  the maximum concentration at saturation and  $k_s$  the constant of reaction at the surface.

- If  $\epsilon$  is very large and/or the rate of dissolution on the surface is high, transport through the boundary layer by molecular diffusion is the limiting step. The rate of dissolution is then controlled by the transport process and can be written as a first-order rate equation (Dreybrodt et al. [9]):

$$R_t = k_t(C_s - C_b) = \frac{D}{\epsilon} C_{eq} (\hat{C}_s - \hat{C}_b) \quad (2)$$

where  $C_b$  is the total concentration of dissolved species in the bulk,  $k_t$  the mass transfer coefficient and  $D$  the diffusion coefficient through the boundary layer. An increase of the fluid velocity will have two effects: the thickness of the boundary layer is decreased and the concentration gradient in the boundary layer becomes steeper.

According to recent studies (Raines and Dewers [10]; Jeschke, Vosbeck and Dreybrodt [11]), the dissolution of plaster of Paris exhibits mixed kinetic control in most common conditions. In this case, both the transport and dissolution process have a significant influence on the rate of dissolution.

### Batch Reactor – Determination of Rates

Using the conservation of the mass in the system, dissolution rates of a solid in a batch reactor can be obtained from the time dependence of the mass concentration by:

$$R = \frac{V}{A} \frac{dC}{dt} \quad (4)$$

where  $V$  is the volume of solution,  $A$  is the total interface area of the plaster and  $C$  the plaster concentration.

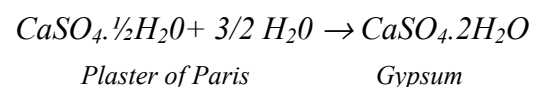
## II. APPARATUS AND EXPERIMENTAL MEASUREMENTS

The aims of the experiments were to generate scallops on the plaster of Paris surface, to measure their geometric and propagation properties and to ascertain the parameters responsible for their various characteristics.

### Materials

Plaster of Paris was chosen as the substrate for these experiments as it has a reasonable solubility and, more important, is easily cast to a suitable size and shape. Moreover, Coney ([12]) has used it to predict the effects of hydrodynamics on the dissolution of pipe walls.

Two types of plaster of Paris were used in this study: a "standard" plaster containing impurities (sand particles) and a "reference" of chemically pure plaster ( $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$  - 98%). Before each experiment the plaster was mixed with deionized water under vacuum for 2 min to avoid the formation of air bubbles and to decrease the porosity of the final gypsum.



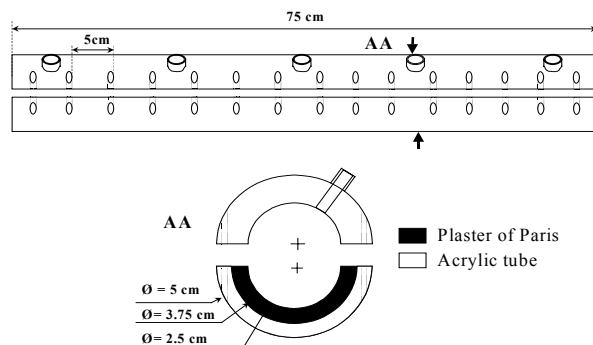
Different moisture ratios,  $R_o$  ( $R_o = M_{\text{Water}}/M_{\text{Plaster}}$ ), were used in order to

optimise the final consistency of the plaster. A ratio of  $R_0=0.6$  was adopted as standard procedure.

Three different sands (mean diameter of 1.5 mm, 0.750 mm and 0.440 mm) were added to the plaster of Paris for a series of tests to study the effect of concentration of included impurity particles.

### Apparatus

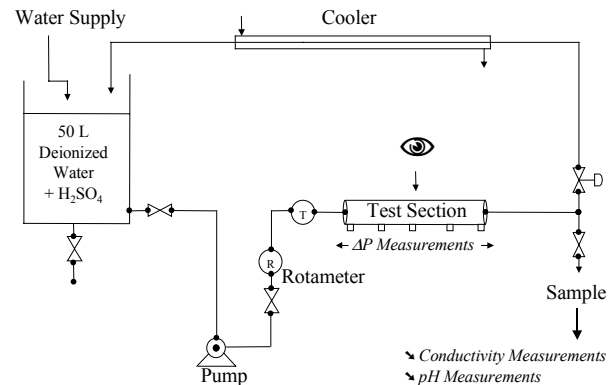
A transparent test section has been designed for this project to allow visual observation of the formation and evolution of scallops. The test section consists of two 75cm-long half-cylinders made of transparent and chemically inert acrylic, that are bolted together with gasket seal of silicone (see Fig.3).



*Fig 3: Design of the test section.*

The bottom part of the test section has a larger diameter than the top part. A layer of mixed plaster, 7.5 mm thick, is poured in the bottom half-cylinder so that the two halves coincide exactly. The test section is installed in a recirculating water loop with compression fittings to avoid any major leak. Fifty litres of deionized water are

initially introduced into the loop reservoir and circulated around the loop by a centrifugal pump capable of generating flow rates up to 14 GPM (see Fig.4).



*Fig 4: Experimental recirculating loop*

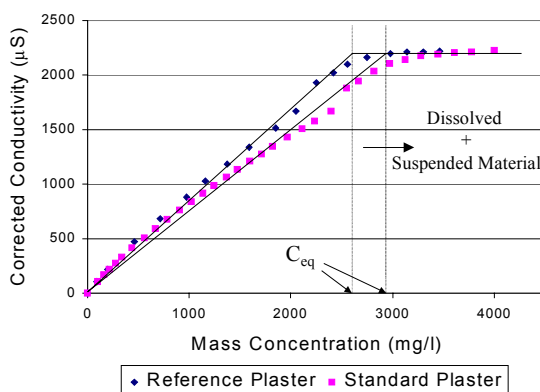
Sulphuric acid (10 ml) is added to the reservoir at the beginning of a run to lower the pH and to prevent the formation of  $\text{CaCO}_3$ . The flow rate is adjusted with a valve and measured with a rotameter. Temperature is recorded at the inlet of the test section during the test and controlled at  $20 \pm 1^\circ\text{C}$  with a water cooler. Samples of the solution are taken at regular intervals throughout a test for analysis.

Different parameters are recorded as indication of the dissolution of the plaster of Paris. The conductivity and the pH of the samples taken are measured during each test. The variations of pressure along the test section are measured with a differential pressure transmitter at the five pressure taps and used for further calculations.

### III. RESULTS AND DISCUSSION

#### Influence of Saturation

To convert the measured conductivity into a mass concentration, the conductivities of gypsum solutions with known concentrations were measured. Known amounts of ground gypsum were added progressively to initially pure deionized water. The corrected conductivity of the solution (corrected conductivity = measured conductivity – initial conductivity of the deionized water) was recorded after each mass increment until the reading was stable. Solid was added until no further increase occurred, even if there were some particles visible in the solution.



*Fig 5: Determination of Saturation*

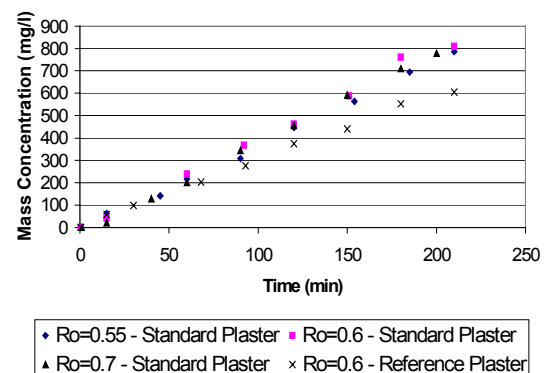
There are two distinct regions visible on conductivity curves in Fig.5. The first, which can be termed the “linear region”, shows an increase of the conductivity with increasing mass concentration of plaster. The conductivity then stabilises to a “plateau region” and becomes constant. By fitting independently the “linear” and “plateau”

regions and finding their intersection, the saturation concentration ( $C_{eq}$ ) can be determined experimentally. Saturation concentrations of 2.60 g/l and 2.97 g/l have been found respectively for the reference plaster of Paris and the standard plaster of Paris. The increase in apparent solubility for the standard plaster of Paris is mainly due to the presence of insoluble impurity particles in the gypsum structure.

Using the extended Debye-Hückel equation to calculate the activity coefficient of the species in solution and the ionic strength, the solubility of pure calcium sulphate has been calculated at 2.58g/l at 20°C, which is close to the experimental value of the reference plaster within 1%. All the experiments have been carried out in the “linear region”.

#### Influence of the Plaster Consistency

Examples of rates of release of calcium ions measured in experiments using different values of  $R_0$  and different types of plaster are shown in Fig 6. All these experiments were conducted at a flow rate of 10 GPM and lasted 3½ h. Rates for the three standard gypsums are similar and higher than that of the reference plaster.

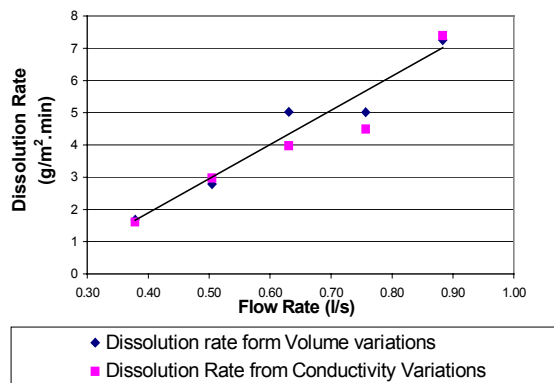


*Fig 6 : Influence of the Plaster composition.*

### Rate of Dissolution of the Plaster

The average rates of dissolution of the plaster of Paris were estimated in two ways:

- First, by measuring the volume of plaster lost by dissolution at the end of the test. This volume was converted to a mass loss and a time-averaged rate of dissolution ( $\text{g/m}^2 \cdot \text{min}$ ) was calculated.
- Then, using the characteristic equations of the batch reactor (Eq.4) and the conductivity measurements, a second rate of dissolution was calculated.



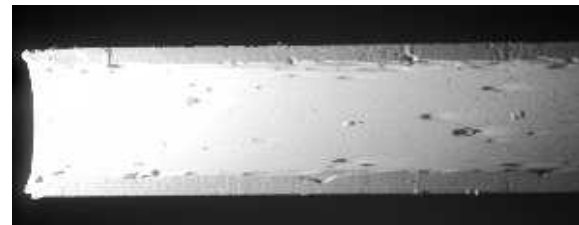
*Fig 7: Plaster Dissolution rates*

The two methods of estimating rates agreed very well (see Fig.7). The rates so estimated at different flow rates exhibited a linear dependence on flow.

### Initiation and Formation of the Scallops

In the first series of tests, the test section was cast with the standard plaster of Paris (ratio  $R_o=0.6$ ). Five different flow rates (6 GPM, 8 GPM, 10 GPM, 12 GPM and 14 GPM) were tested. Flow conditions in the test-section were turbulent at all flow rates and Reynolds numbers varied from 12500 at 6 GPM to 44000 at 14 GPM. The

observation of the plaster surface at the end of a run showed clearly the presence of scallops. Observations throughout the run indicate that the population of scallops continuously increased.



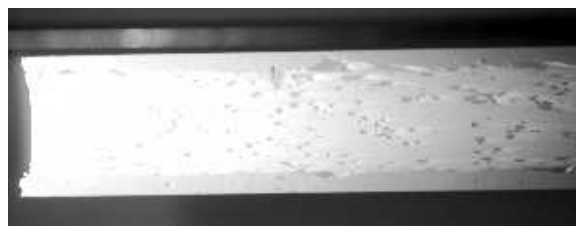
No sand – Reference Plaster of Paris



Sand Particle  $D_p=1.5$  mm– Reference Plaster of Paris



Sand Particle  $D_p=0.750$  mm– Reference Plaster of Paris



Sand Particle  $D_p=0.440$  mm– Reference Plaster of Paris

*Fig 8: Final aspect of the test-section after a 3½h run at 10 GPM.*

The second series of experiments was done with the chemically pure reference plaster with the same standard  $R_o$  value of 0.6. This time, however, the plaster surface



developed no scalloping. The only erosion marks observed were initiated at air bubbles present in the subsurface and revealed by the dissolution.

The main difference between the plaster types in the first and second series of experiments is the presence of impurity particles in the standard plaster. To increase the number of scallops at the surface of the pure reference plaster, three different tests were carried out, in which sand particles of known diameter (1.5 mm, 0.750 mm and 0.440 mm) were added to the plaster. These impurities were introduced in a homogeneous way during the mixing of the plaster. The amount of sand added was adjusted to get a concentration of 20 particles/cm<sup>3</sup>. The results after exposure in the loop (Fig.8) showed the presence of scallops on the surface all along the test section.

The postulate that the presence of an initial defect at the surface is responsible for the formation of a scallop is therefore supported, confirming the *defect theory*.

### **Surface Density of the Scallops**

At high flow rates, the scallops initially appeared at the inlet of the test section and then propagated downstream. At lower flow rates, the observation of this phenomenon was more difficult; nevertheless, it seems reasonable to affirm that the phenomenon occurs at every flow rate.

The surface density of the scallops increased with increasing flow rate. Fig 8 shows that the number of defects present in the plaster matrix played an important role in the formation of the scallops; the more defects there were in the plaster structure,

the more scallops were seen at the end of the test. As the overall dissolution of the plaster increased with flow, defects present initially in the plaster came to the surface more quickly and led to scallops.

### **Size of the Scallops**

Post-test observation of the plaster showed that the average size of scallop decreased as the flow increased.

The size of the defect also influenced scallop formation. At a given flow rate, smaller sand particles produced smaller scallops.

### **CONCLUSION**

The studies carried out on the dissolution of plaster of Paris conduits showed that:

- the marks of erosion (scallops) initiate at a surface defect .
- they initiate up stream and progressively form downstream.
- their size and number depend on the water flow rate. The number of scallops increases with the flow rate whereas the average size of a scallop decreases with flow rate.
- the rate of dissolution of plaster is proportional to the water flow rate.

A quantitative analysis of the formation and evolution of scallops is in progress using a phenomenological model developed by Santarini [13,14]. This provides a description of surface evolution up to a limit where two scallops meet.

## NOMENCLATURE

A	Total surface area, (m <sup>2</sup> ).
CaSO <sub>4</sub> .1/2H <sub>2</sub> O	Plaster of Paris.
CaSO <sub>4</sub> .2H <sub>2</sub> O	Gypsum.
C	Plaster concentration, (g/m <sup>3</sup> ).
C <sub>b</sub>	Total concentration of dissolved species in the bulk, (g/m <sup>3</sup> ).
$\square_b$	C <sub>b</sub> /C <sub>eq</sub> .
C <sub>eq</sub>	Saturation concentration, (g/m <sup>3</sup> ).
C <sub>s</sub>	Total concentration of dissolved species, (g/m <sup>3</sup> ).
$\square_s$	C <sub>s</sub> /C <sub>eq</sub> .
D	Diffusion coefficient, (m <sup>2</sup> /s).
ε	Boundary layer thickness, (m).
k <sub>s</sub>	Constant of reaction at the surface, (g/m <sup>2</sup> .s).
k <sub>t</sub>	Mass transfer coefficient, (m/s).
R <sub>s</sub>	Surface-controlled dissolution rate, (g/m <sup>2</sup> .s).
R <sub>t</sub>	Transport-controlled dissolution rate, (g/m <sup>2</sup> .s).
R	Effective dissolution rate, (g/m <sup>2</sup> .s).
V	Total volume of solution, (m <sup>3</sup> ).
R <sub>o</sub>	Plaster mix ratio.

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