Description of the Deliverables

Demonstrator-Experimental Data from the Application domain

- Experimental data from the application domain (Demonstrator) that are to be used in the Environment Simulator should be collected and the physical principles modeled in detail.(UOP)

1. Experimental Measurements

1.1. The Problem: The simulator and related measurements were done in a way that the basic scenario may be implemented. According to the scenario, th scale formate problem is the initiation of scale formation in quiescent aqueous medium in steel tanks or pipes used as bypass loops in the oil production industry. The mineral components of scale deposits depend strongly on the chemical composition of the water used but in most cases it consists of calcium carbonate ($CaCO_3$). The formation of this mineral is favored by the high content of natural water in calcium salts and dissolved carbonate species[1]. The formation of this salt may be described by reaction (1):

$$Ca^{2+}(aq) + HCO_3^-(aq) \rightarrow CaCO_3(s) + H^+ \quad (1)$$

The protons released from this reaction result in changes of the physicochemical parameters of the aqueous phase in contact with the steel wall of the reservoirs and/or pipes and promote corrosion which occurs at a later stage according to the scheme of reactions (2)[2]:

$$\begin{array}{lll} & 2H^+ + 2e^- \rightarrow & H_2(g) \\ & Fe \rightarrow & Fe^{2+} + 2e^- \\ & \underline{Fe^{2+} \rightarrow} & \underline{Fe^{3+} + e^-} \\ 2H^+ + Fe & \rightarrow & Fe^{3+} + H_2(g) + e^- \qquad (2) \end{array}$$

As may be seen, the scale formation process is coupled with corrosion. Early detection and remediation therefore of scale formation is imperative as it may prevent or eliminate corrosion as well. **Early detection of the scale formation process offers the advantage of savings in monitoring and at the same time making it more effective**. The practice today in the industry is to use different monitors for corrosion consisting mainly of platinum electrodes responsive to potential changes concomitant with the reaction (2) involving the ferric/ferrous species.

The main advantage of the possibility of monitoring scale formation processes occurring according to reaction (1) is the availability of sensitive and fast responding sensors for the H^+ activity in solutions (pH electrodes). These sensors have typically response times 1-2 s and their sensitivity may range between 0.1-0.5 mV. The latter is typical for ISFET sensors which offer the possibility of implementation in the SNN agents to be constructed for the purposes of the present project. It should be noted that 1 pH unit change corresponds to 60 mV. During a cycle of calcium carbonate scale deposition the variation of the solution pH in a time period of one hour is usually in the order of 70 mV (more than 1 pH unit change). The initiation of scale formation is usually accompanied by relatively high rates of pH change [3-8]. A threshold of 0.5 mV change in the vicinity of the initiation of scale deposits formation is realistic and corresponds to a variation of pH by approximately 0.01 units.

The most interesting feature of this concept is that the agents shall have the possibility to exert premeditative action with t the very initial stages of the fault development. Because of the fact that fault generation is due to the formation of a proton generating salt it is possible that the K agents upon approaching the fault point they may infuse an effective scale formation inhibitor which shall result in stopping the process right at the initial stages. A large variety of efficient inhibitors is available in the market [1]. Oragnophosphorus compounds is a very successful group of compounds which is efficient inhibitor for the growth of a number of sparingly soluble salts, calcium carbonate included [9-13]. The list of this type of compounds is ever increasing [14]. The practice so far in the industry is to add the appropriate quantities in the bulk of the water to be treated. As a result of the fact that the action of the scale formation inhibitors is not localized larger quantities are needed and consequently the treatment cost is increasing. Moreover, since in most of the cases these compounds are toxic their disposal after use is also a problem. The obvious advantage in our approach, i.e. the delivery of the inhibitor by an agent, is that the action shall be localized and hence more efficient resulting in the use of very low quantities of the inhibitors. It is estimated that only a small fraction shall be needed in comparison to the normal application. The obvious advantages resulting shall be **reduction in operational cost and minimization of environmental hazards**.

1.2. Laboratory Measurements

A complication arising from the fact that the aqueous media we are concerned with are stagnant (or quasi-static) , implies that the composition is not uniform throughout the bulk water. pH gradient is developed as a result of the fault (scale initiation process). Measurements of the spatial distribution of the diffusing protons are needed, for the definition of the response of K agents. The measurements were done in two different types of laboratory bench experiments:
(i): As a function of depth in a vertical water column
(ii) Longitudinal diffusion in a shallow vessel .
In setup (i) a cylindrical vessel of inner diameter of 7cm and 50 cm length was filled with an aqueous medium. A special construction made of PVC was constructed to allow the immersion of a pH sensor (Vernier Inc. USA) consisted of two pieces which could be connected, the two parts being sealed with an O-ring to ensure water proof conditions for the sensor at variable depths in the cylinder. The sensor had an amplifier incorporated in the plastic body encasing it and was connected via a n A/D-D/A converter with a PC and the solution pH was monitored as a function of time(Figures 1 and 2). Proton generation was created at the top of the water column and pH was recorded by changing positions of the sensor. pH-time profiles were thus recorded (see Appendix I), which were next converted into potential-distance profiles as shown in the results section.

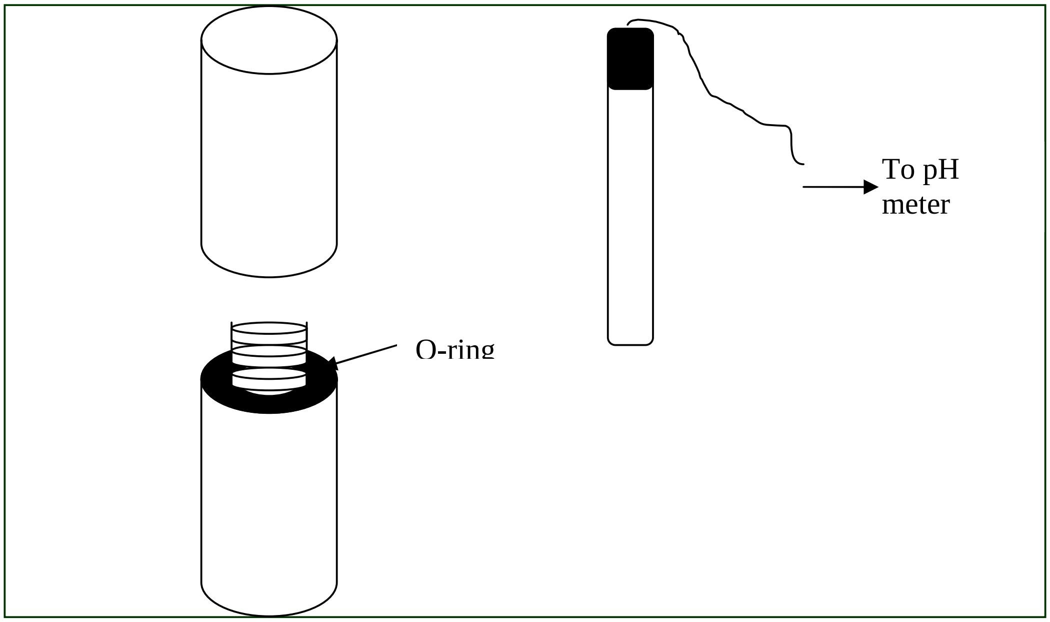


Figure 1: Holder for the measurements done at variable depths in a water cylinder

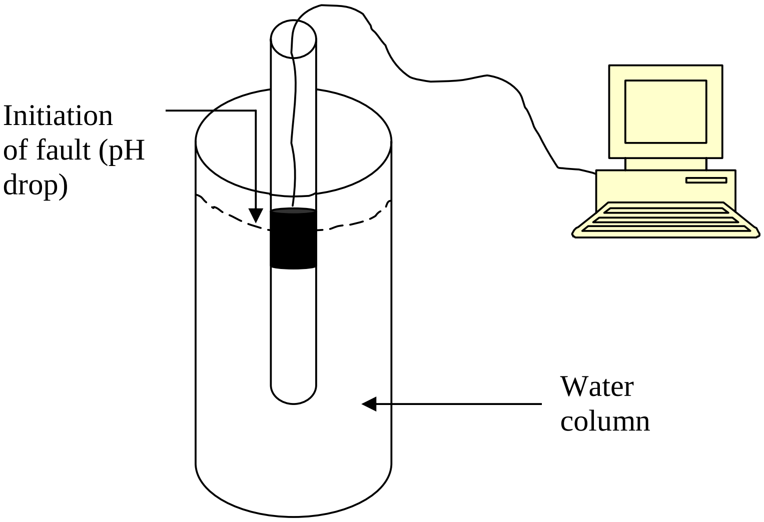


Figure 2: Experimental set-up for recording pH at different immersion depths with respect to the fault initiation (H^+ ion release)

Alternatively the variation of pH with distance was measured in a tank using 4 pH sensors connected through a LabPro® interface to a computer with the appropriate software for Data acquisition (Data Loger 3.0, Vernier Inc.) as shown in Figure 3:

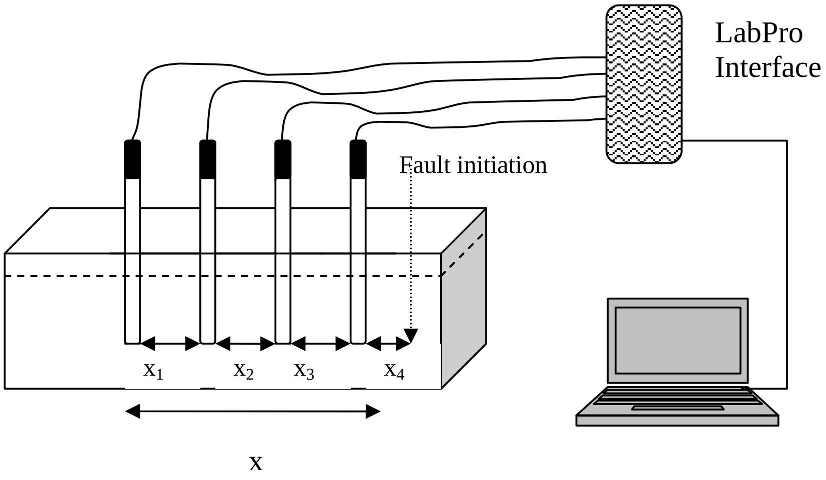
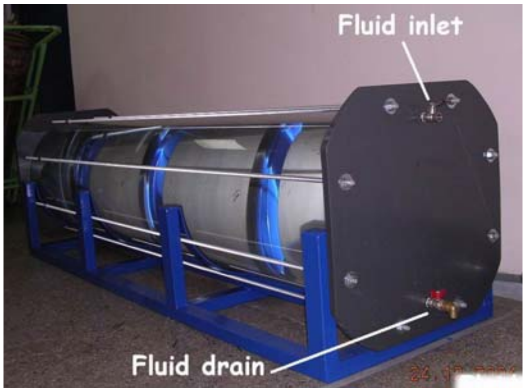


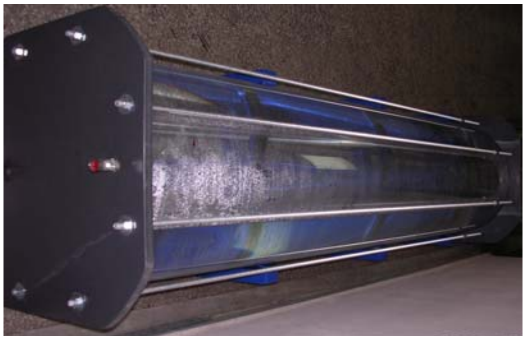
Figure 3: Experimental set-up for recording pH at different distances with respect to the fault initiation (H^+ ion release). Sensors are immersed to same depth.

1.3. Construction of the demonstrator

The simulator for the testing of the agents has been constructed. It consists of a Plexiglass™ tube, 2m long and 50cm inner diameter. The device shall be be placed in the floor because of the weight. A metallic frame work was constructed having four semi-cylindrical supports lined with special cushions to dissipate the fluid weight. The sides at the two ends of the cylinder were secured by special stainless steel bars running horizontally and tightened with the appropriate 500 mm O-rings to the PVC plates used as caps of the two cylinder sides. Measurements of pH distance profiles before the deployment of the agents shall be done through the appropriate openings at stationary conditions using the sensors, interface and computer system shown in figure 3. The construction is shown in figure 4:



side view



View from top

Figure 4: Simulator for the agents testing in a static fluidic environment

Ports for the introduction of the agents and for preliminary measurements of the pH variation as a function of the distance from the signal initiation point shall be available on the top of the testing tube system as shown in figure 5

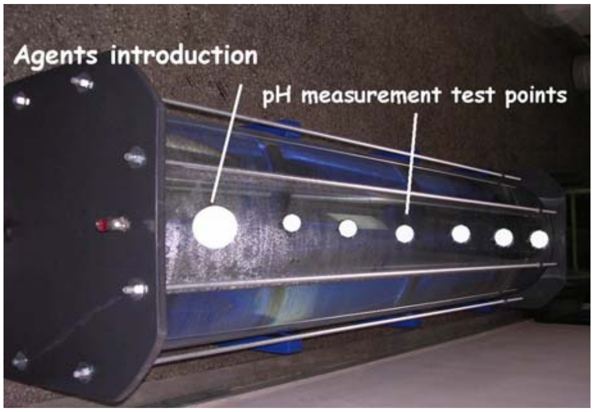


Figure 5: Ports on the simulator or the introduction of the agents and of pH sensors

2. Results

2.1.Experimental measurements of the output of the pH sensor (signal in mV) as a function of the distance from the fault source (generation of H+ ions)

The recording was done in the tank shown in figure 3, using 4 sensors located at 2, 4, 6 and 8,5 cm from the point of generation of a concentration of H+ ions. The signal-time plots obtained were as:

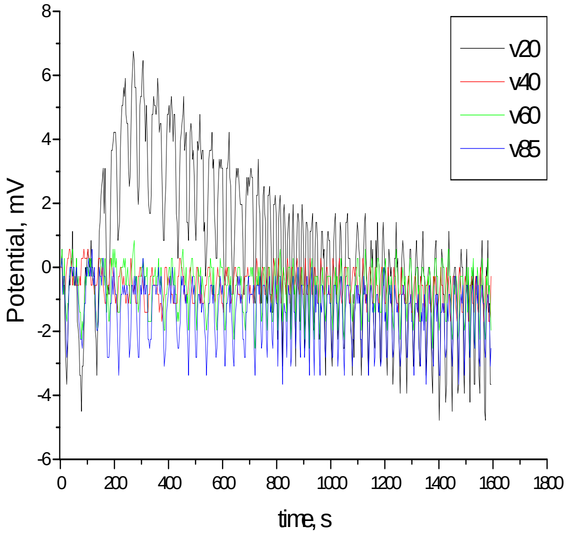


Figure 6: Change in the signal in the four sensors following the addition of 0.02 ml HCl 1M

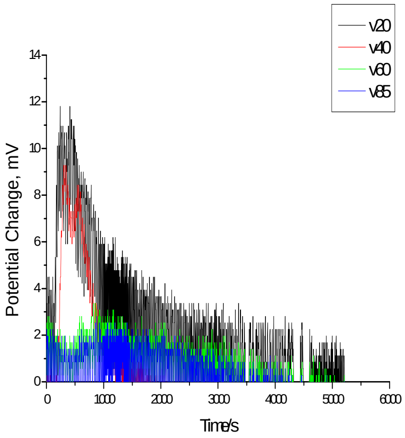


Figure 7: Change in the signal in the four sensors following the addition of 0.2 ml HCl 1M

From the recordings shown in figures 6 and 7 the signal-distance profiles were obtained and they are shown in figures 8 and 9 respectively:

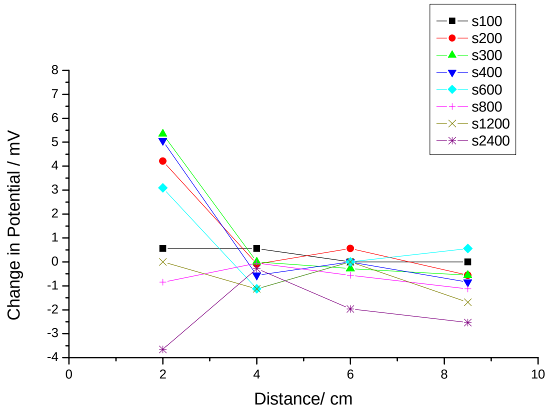


Figure 8: Change in the signal in the four sensors as a function of the distance from the fault source, i.e. the addition of 0.02 ml HCl 1M. Insert shows distances in mm.

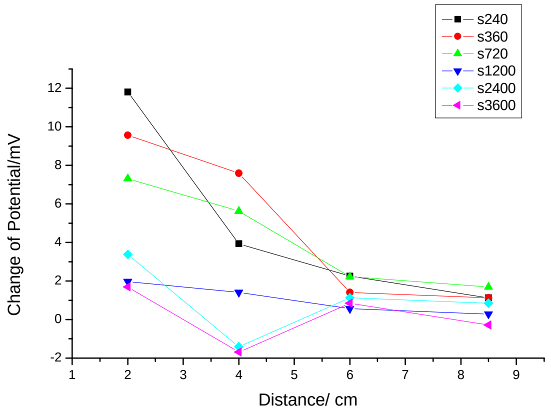


Figure 9: Change in the signal in the four sensors as a function of the distance from the fault source, i.e. the addition of 0.2 ml HCl 1M. Insert shows distances in mm.

Additional measurements in the same system yielded similar results as may be seen in figures 10 and 11:

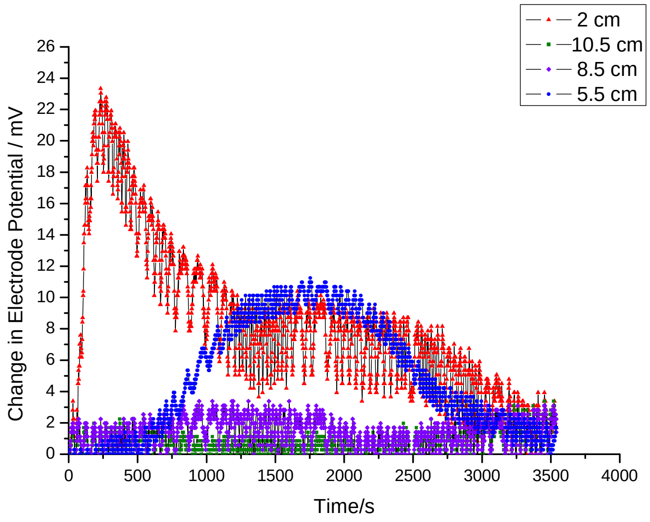


Figure 10 : Change in the signal in the four sensors as a function of time starting from the generation of fault, i.e. the addition of 0.2 ml HCl 1M. Insert shows distances in mm.

From the profiles shown in figure 10 and for times equal to 200, 360, 600, 1200 and 3600 s, the signal-distance profiles were obtained and they are presented in the figure 11:

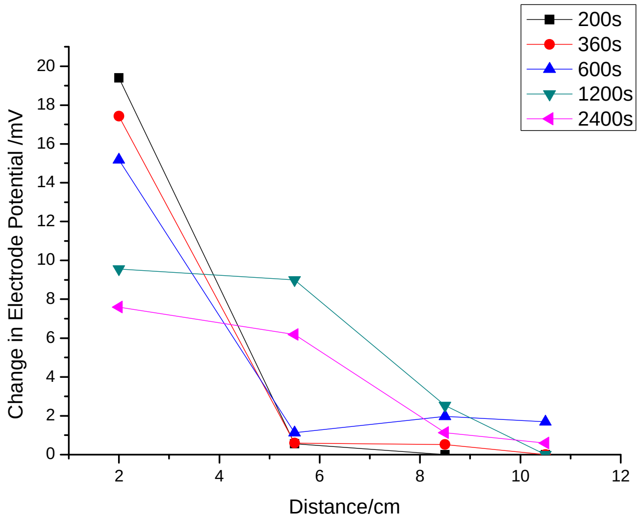


Figure 11: Change in the signal in the four sensors as a function of the distance from the fault source, i.e. the addition of 0.2 ml HCl 1M. Insert shows distances in mm.

2.2. Measurements of signal detected by sensors placed inside an aqueous solution cylinder at different depths/distances from acid generation process

The aqueous medium was selected with a composition allowing for relative pH stability. Thus the aqueous medium consisted of KH_2PO_4 (m=0,0087) and Na_2HPO_4 (0,030)[m=molality, mol Kg^{-1}] yielding an approximate pH value of 7.00. The fluid was contained in a 1Liter graduated cylinder. A special construction was used which allowed to vary the location of the sensor in the fluid column. The aqueous medium was not stirred allowing for static conditions.

The choice of an aqueous medium with constant pH, close to neutral is a better simulation of natural waters buffered by their carbonate content. At the surface of the aqueous solution a small aliquot (20 μl) of concentrated hydrochloric acid was introduced. Typical results obtained from the experiments at static conditions yielded the following results:

For a distance of 29.5 cm (Acid introduction – sensor location)

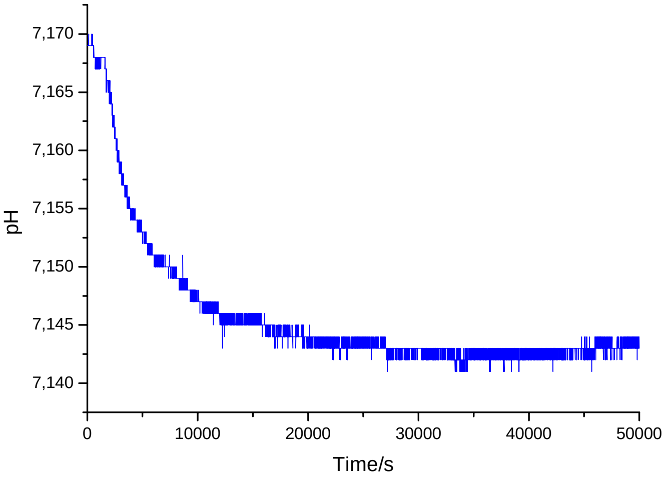


Figure 12: pH-time profile for 29.5 cm distance of sensor from the signal generation

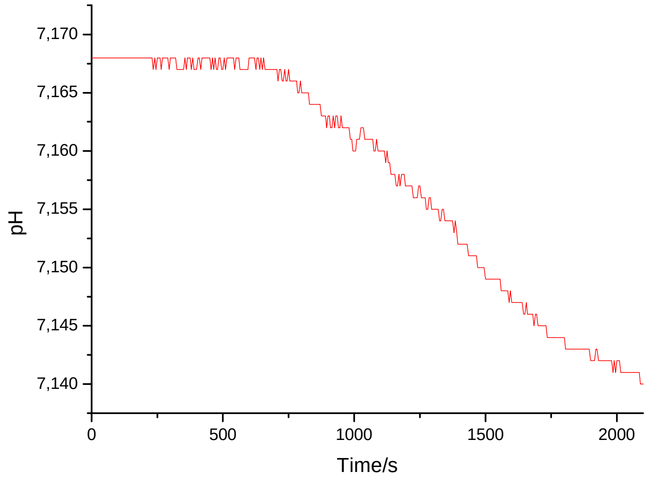


Figure 13: pH-time profile for 19.5 cm distance of sensor from the signal generation

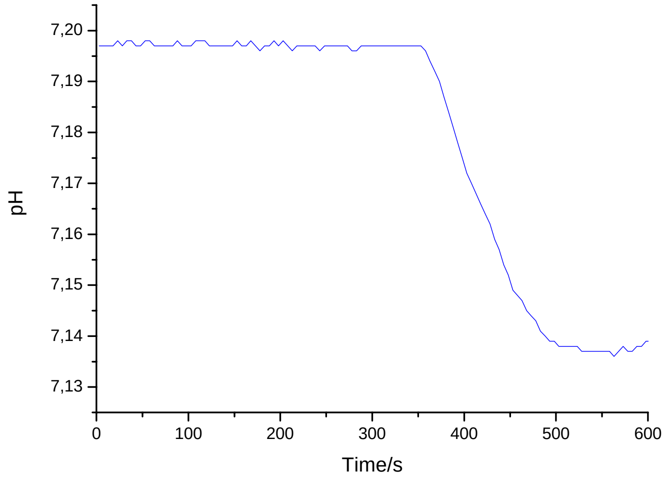


Figure 14: pH-time profile for 6.5 cm distance of sensor from the signal generation

If a fluid flow is imposed on the system the time scale between signal generation and sensor recording shall be significantly shortened.

Similar results have been observed with tap water experiments. It should be noted however that in this case the noise level was higher because of the lower buffer capacity of the aqueous medium.

In the next series of experiments which are currently carried out a less strong buffer consisting only of Na_2HPO_4 system is used in which the pH changes anticipated are much sharper. In this case a weaker acid (0.1N HCl) shall be used to avoid any density gradients. In the series of experiments presented here (Figures 12-14) density gradient may also be a factor affecting the response time of the sensor as a function from the distance of the signal generation.

Te variation of the signal as a function of distance from the point of generation of the signal (pH drop) past a time lapse of 500s (initial pH 7,196) is sown in figure 15. It sould be noted that past this time, the sensor at the first position (6.5cm from the source) reached a plateau value (7,139)

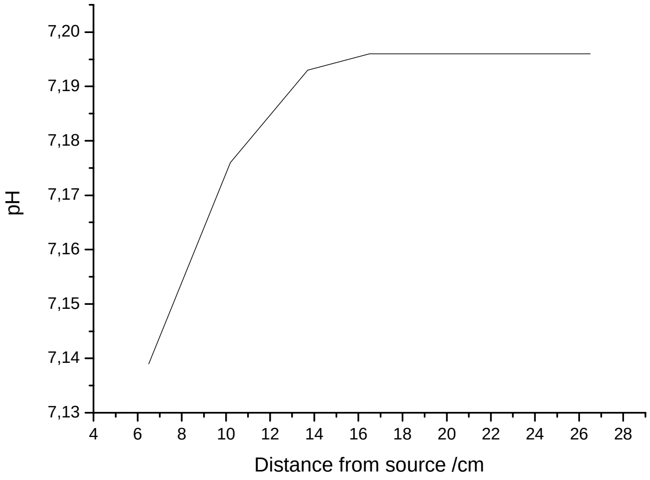


Figure 15: Dependence of the signal on the position of the sensor from the source of signal generation (readings taken 500 s past the acid spike on the top of the static fluid).

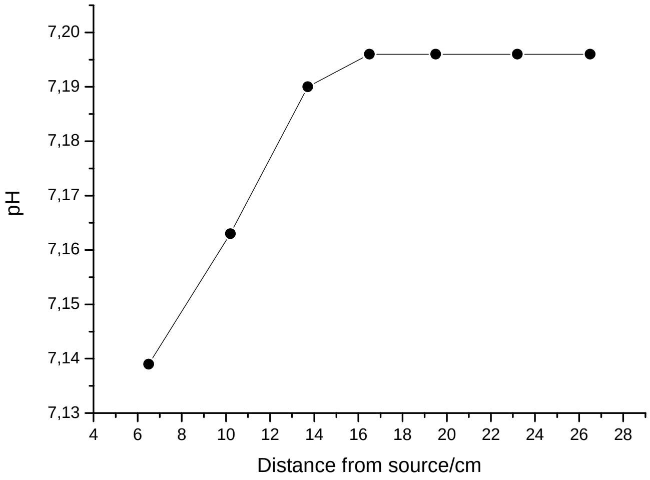


Figure 16: Dependence of the signal on the position of the sensor from the source of signal generation (readings taken 1000 s past the acid spike on the top of the static fluid).

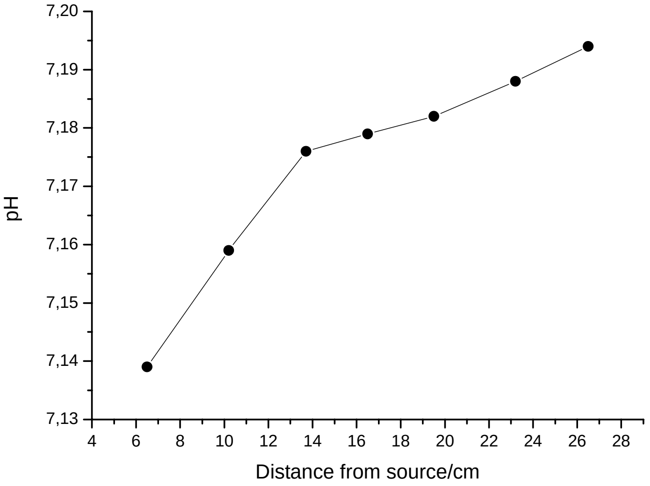


Figure 17: Dependence of the signal on the position of the sensor from the source of signal generation (readings taken 2000s past the acid spike on the top of the static fluid).

Note: For the construction of the pH-distance plots a correction to the pH readings has been applied so that readings start from the same point

2.3.Modelling the variation of pH

The process of H^+ and the concomitant signal variation from the sensors may be assumed that is described by diffusion.

The solution to Fick's 2nd Law of diffusion for the case of a point source, U_o [units], deposited at zero time (t = 0) at the origin (r = 0) is C(r,t) [units cm^{-3}]:

$$\mathbf{C(r,t)} = \mathbf{U_o} \frac{\mathbf{exp}\left(-\frac{\mathbf{r^2}}{\mathbf{4\chi t}}\right)}{(4\pi\chi t)^{3/2}}$$

where r [cm] is the distance from the source to the point of observation, t [s] is the time of observation, and [cm^2/s] is the diffusivity. In the denominator, the product t has units of [cm^2] which is taken to the 3/2 power to yield units of [cm^3]. The exponential in the numerator is dimensionless. The units of U_o can be the units of any extensive variable which is able to diffuse throughout a volume. Hence, C(r,t) has the proper dimensions for concentration, [units cm^{-3}]. The above expression for C(r,t) is a solution to Fick's 2nd law of diffusion and describes spherically symmetric diffusion from a point impulse source in a homogeneous medium with no boundaries. Diffusivities of aqueous species is of the order of 1-2 $x10^{-9}$ m^2s^{-1}
The generalized Fick's 2nd law for 3 dimensions is expressed as:

$$\frac{\partial c}{\partial t} = D\left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2}\right)$$

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