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Control of Corrosion and Scaling in Selected Geothermal Wells from Romania

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ABSTRACT

Aquifer fluid compositions have been determined by analysis made on water samples collected from production wells in Felix geothermal area from Romania. Data acquired was used in reservoir monitoring of the field to forecast chemical changes.

In order to assess the corrosion processes in exploitation equipments there were determined the corrosion rates, for geothermal waters from all the studied wells. By analysing the tests results, it was found out the necessity of using additives for corrosion at two of the wells. The present paper will indicate the studies performed with corrosion inhibitors, monitoring their efficiency.

The state of mineral saturation of the geothermal waters with respect to different minerals was studied by simulation program. Diffraction analysis was done for solid samples from the wells where scales were formed during utilization. They were made tests with additives, in static conditions, ones to check the good performance of additives to avoid deposition formation and a second method assumed to measure the change in pressure across a capillary tube in conditions of using different dosage of additives. The greater the time to reach an increase of pressure, the better the additive at controlling deposition.

1. INTRODUCTION

Renewable energy has been promoted over the past decade. Romania has a good geothermal potential, especially in the western part of the country, where have been exploited low-temperature geothermal wells.

The major problem encountered at production of the wells is the scale on the heat transfer surfaces, which results in a serious loss of efficiency and production. Without effective scale control, this can lead to the eventual shutdown of the production for cleaning.

This paper presents the research results obtained for four geothermal wells located in Baile-Felix resort, nearby Oradea. They are the following: 4003, 4011, 4012 and Balint. These wells supply geothermal water for heating hospitals, hotels and commercial buildings and for swimming pools from the local community.

The corrosion and scaling problems suggested the necessity of laboratory investigations.

The first objective was to get the chemical composition of these waters and then to determine the corrosion rate and the scale deposits and to try to find out the best additives which control corrosion rate and deposition formation from mineral precipitation.

2. EXPERIMENTAL PROCEDURES

2.1 Chemical Characteristics of Geothermal Waters

Waters from the four geothermal wells were sampled and the main components were analysed in the laboratory by the methods briefly presented in table 1 and in details in (Stănăşεl et.al, 2006). The wellhead temperatures measured during collection of water samples were 40-42ºC.

Table 1: Methods of water analysis

Constituent	Type of analysis
Cl^-	Volumetric
HCO_3^-	Volumetric
CO_3^{2-}	Volumetric
SO_4^{2-}	Chromatography
NH_4^+	Volumetric
Ca^{2+}	Volumetric
Mg^{2+}	Volumetric
Fe^{3+}	Spectroscopy in VIS
Na^+	Flamphotometry
K^+	Flamphotometry
SiO_2	Spectroscopy in VIS
pH	Electrometric
Mineralization	Gravimetric

2.2 Corrosion Rates Without and in Presence of Additives

In order to determine the corrosion rates, in the presented paper it was used the gravimetric method, in static conditions for the four wells and also in dynamic conditions for well 4011. Corrosion tests were conducted using carbon steel coupons, like the pipe material exposed to fluids from Felix wells. The metal coupons were treated first with a solution of 10% HCl, washed with distilled water, alcohol and dried. The measured surface of the coupons was 0.00165 m^2. The coupons were weighed to 0.001 g accuracy before introducing them into the test. The water bath was kept at constant temperature of 25ºC, respectively 40ºC. The measurements were done for periods ranging between 360 and 2040 hours. Changes in weight after immersion in the geothermal water were used to determine the effects of corrosion for each coupon.

In lab conditions was studied the action of additives from precipitation and adsorption type, by the use of gravimetric method. The coupons were from the same material as the pipe. The method for preparation of the coupons and the timing was the same as in the case without any treatment.

As anti-corrosion additives were used disodic phosphate (Na_2HPO_4) and tiouree (CH_4N_2S). There were used different concentrations of additives, trying to find out the minimum dosage needed to prevent corrosion.

2.3 Chemical Deposition Control

A laboratory test was made to control the calcium carbonate deposition. The geothermal water from well 4003 was pumped at constant flowrate through a stainless steel capillary tube immersed in water bath at 40^0C. Any calcium carbonate deposition reduces the bore of the tube and is followed of an increase in pumping pressure. The rate of change in pressure across the capillary tube was monitored by a pressure traducer and plotted against time on a chart recorder. A tripolyphosphate additive was maintained at 2 mg/l during the test and the time to reach a pressure difference of 0.07atm was measured. There were used different dosages of additive. The greater the time reaching that change in pressure, the best the additive. The same experiments were done with a copolymeric additive.

3. RESULTS AND DISCUSSIONS

3.1. Chemical Characteristics of Geothermal Waters

Table 2: Chemical composition of studied waters, in mg/l

Constituent	Well			
	4011	4012	Balint	4003
Cl^-	26,59	17,73	26,59	21,28
HCO_3^-	396,5	396,5	427	500
SO_4^{2-}	287,8	189,3	485,2	89,3
NH_4^+	0,084	0,07	0,114	0,065
Ca^{2+}	170,6	110,9	136,4	123,6
Mg^{2+}	35,4	41,4	139,7	27,8
Fe^{3+}	0,0128	0,138	0,0108	0,0152
Na^+	16,2	8,6	19,5	17,4
K^+	4,7	2,4	5,6	4,8
SiO_2	23,2	11,7	38,3	15,7
pH	6,5	6,4	7	7
Mineralization	685	392	638	490

As seen from Table 2, the studied waters can be classified as calco-bicarbonated waters. It can be anticipated calcium carbonate deposition in exploitation equipments. Mineralization is higher at geothermal waters from wells 4011 and Balint, being 0.6-0.7 g/l. The pH is neutral, respectively weak acid at waters from wells 4011 and 4012. The high carbon dioxide content, which at the waters' pH is especially in the form of bicarbonate, associated with the chloride content, gives a tendency of corrosion of the pipes, that could be amplified of the water temperature around 40^0C at the wellheads. The presence of oxygen constitutes a major danger in corrosion process.

3.2 Results of Corrosion Rates

Calculation data for the corrosion process of the coupons immersed in geothermal water from well 4003 are summarized in table 3. The results of the corrosion processes for the other wells are illustrated in Figure 1 for well 4011, comparative in static and dynamic conditions and in Figures 2 and 3 for wells 4012 and Balint in static conditions.

Table 3: Corrosion rate results, well 4003

Temp, [ºC]	Weight loss, [g]	Exposed time, [hours]	Corrosion rate, [g/m^{2}hour]	Corrosion rate, [mm/year]
40	0,1505	360	0,25333	0,2812
	0,1319	576	0,13874	0,1540
	0,1053	720	0,08865	0,0984
	0,0515	1080	0,02892	0,0321
	0,0544	1440	0,02288	0,0254
25	0,1361	360	0,22910	0,2543
	0,1074	576	0,11297	0,1254
	0,0958	720	0,08063	0,0895
	0,0478	1080	0,02685	0,0298
	0,0417	1440	0,01757	0,0195

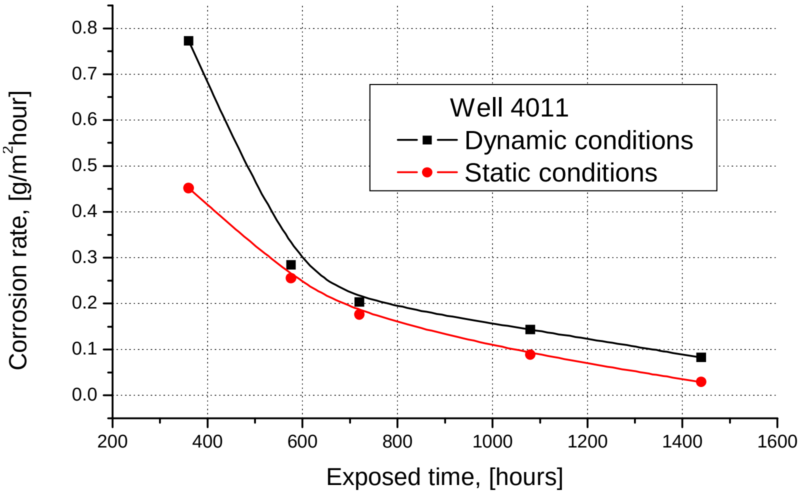

Figure 1: Changes of corrosion rate in time, at 40 C.

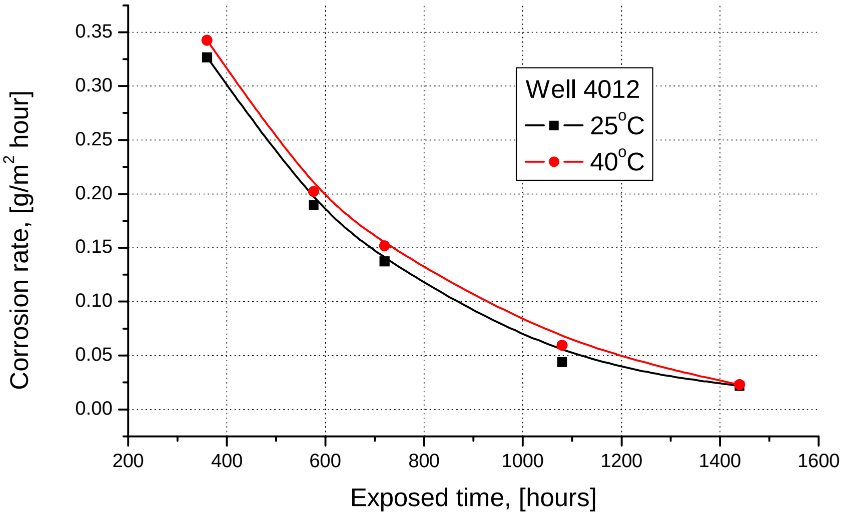

Figure 2: Changes of corrosion rate in time

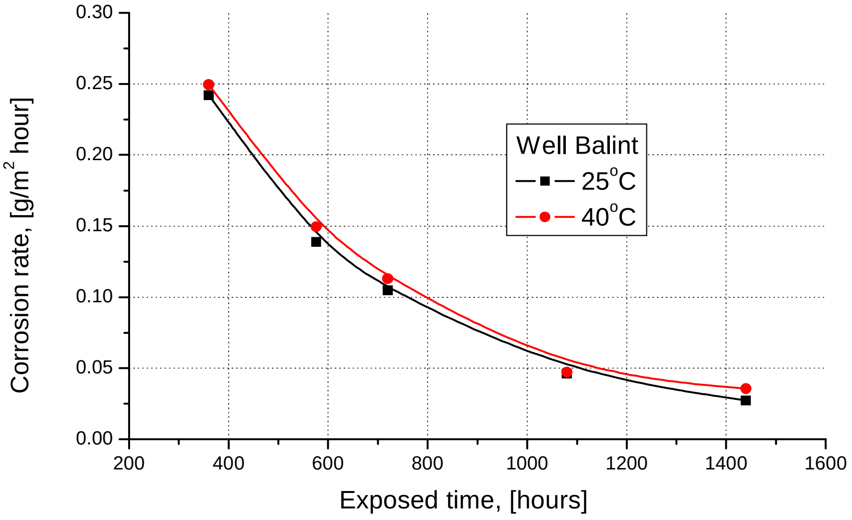

Figure 3: Changes of corrosion rate in time.

You can notice the strongest corrosion process of the coupons exposed in geothermal water from well 4011, followed by well 4012 and comparable values are observed at wells 4003 and Balint. The corrosion process is more accurate in the first month of testing at all the wells. The corrosion process decreases in time, being almost stable in the second month, which is probably due to corrosion products, with a passive action, formed on the coupons surface. Experimental it was recognized a uniform corrosion in the first half of testing period and later then a tendency to pitting corrosion.

The data from Figure 1 regarding the tests for well 4011, made at the wellhead temperature, indicate almost a double corrosion rate in dynamic conditions compared to static ones.

3.3. Protection with Anti-Corrosion Additives

In Figures 4 and 5 are shown the experimental results obtained in static conditions regarding the influence of the two anti-corrosion additives effects on corrosion rates in time. The temperature of geothermal water was maintained at 40 C.

It was calculated the efficiency of chemical protection with anti-corrosion additives, by the use of equation:

$$E_p = \frac{v - v_1}{v} \cdot 100, \ [\%]$$

Where v represent the corrosion rate without additive, and v_1 represent the corrosion rate in presence of additive, in g/m^2hour.

The results are summarized in tables 4 and 5.

Table 4: Efficacity protection with different concentration of two additives, well 4003, in%

Na_2HPO_4			CH_4N_2S.		
25 ppm	50 ppm	100 ppm	25 ppm	50 ppm	100 ppm
66.6447	83.3816	91.6711	34.3947	55.7500	71.5395
64.3070	89.0442	94.7383	33.6162	53.0052	69.6552
59.7287	87.3659	94.9238	28.4817	52.2835	73.3780
67.8411	84.0935	91.0093	55.0467	68.1869	79.5981
68.5354	83.7870	95.1929	61.1063	72.4685	81.6457

Table 5: Efficacity protection with different concentration of two additives, well 4011, in%

Na_2HPO_4			CH_4N_2S.		
25 ppm	50 ppm	100 ppm	25 ppm	50 ppm	100 ppm
52.7119	75.1519	82.8428	28.7741	48.8186	67.9092
50.3165	62.8175	83.3363	29.8347	46.7937	53.1847
48.9580	77.0787	87.9002	29.0926	44.2160	57.7927
66.0000	88.4400	89.3161	18.7538	43.4316	46.2432
66.0000	71.3631	89.0708	26.5846	68.5785	71.9938

3.4. Fluid-Mineral Equilibriums

An assessment of potential scaling problems can be obtained through interpretation of the analytical data from Table 2. Using the Watch simulation program, log solubility (logQ) for the minerals was calculated. The program also reports the theoretical log K by temperature for the corresponding minerals. Then there were plot the saturation indexes (logQ/K) for different minerals against temperature (Figure 6), starting at the wellhead temperature and then at lower temperatures, which can be reached during geothermal water utilization.

The logQ/K diagram for water from the well 4003 indicates a little supersaturation with respect to calcite and at the wellhead temperature you can notice a chalcedony suprasaturation. Talc is supersaturated, being estimate a silica deposition in crystallization form. The other minerals are undersaturated. So, there is a possibility of calcium carbonate crystals and quartz.

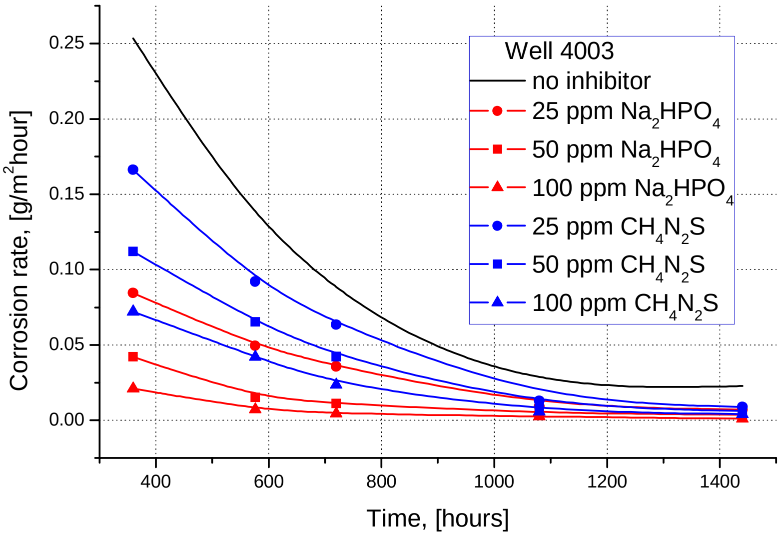

Figure 4: Changes of corrosion rate in time, well 4003.

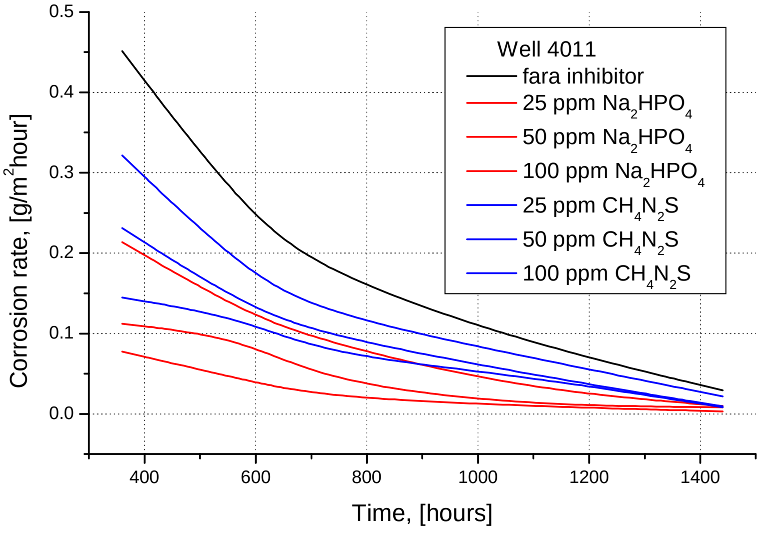

Figure 5: Changes of corrosion rate in time, well 4011.

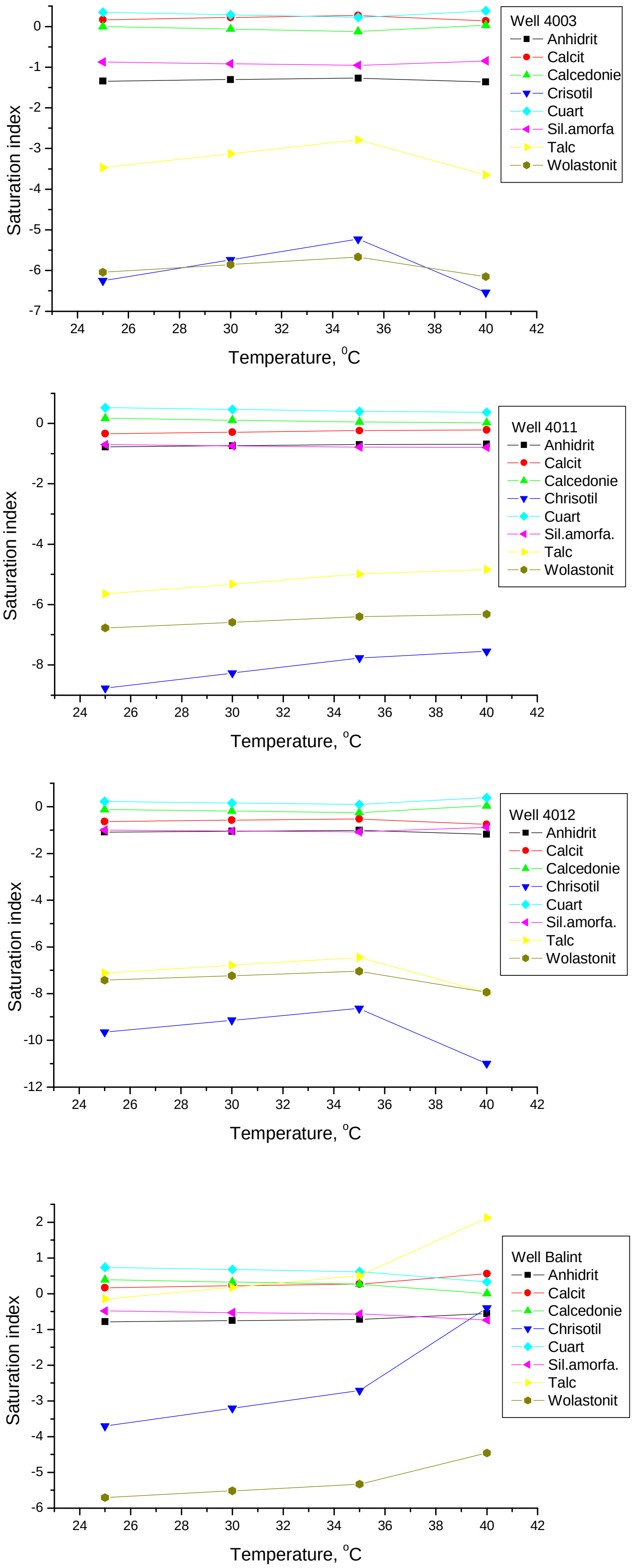

Figure 6: Fluid-mineral equilibrium diagrams

Regarding well 4011, the saturation index of quartz is around 0.5, that could indicate a possible crystallization of this mineral. There is an equilibrium with chalcedony, the rest of the minerals do not record any possibility of deposition.

For well 4012 quartz presents a supersaturation, which decreases at lower temperatures than the wellhead one.

At Balint well appears a calcite supersaturation at all the temperatures. Quartz presents a supersaturation which increases by temperature decreases. The high saturation index of talc does not indicate problems, because this mineral has no adherence at pipes, especially during well production.

3.5. Structural Deposition Analysis

In order of getting information about the crystals in the solid sample from well 4003, the XRD studies were made by using a PHILIPS PW 1400 X-ray spectrometer with KαCu radiations. The X-Ray diagram is presented in Figure 7.

The results of X-Ray diffraction analysis indicates the presence of calcite crystals and of quartz in the sample from well 4003.

3.6 Calcium Carbonate Deposition Control

It was found out (Figure 8) that the phosphate additive gives better results. It can be used in concentration of 12 mg/l compared with the other, which is efficient at higher concentration.

4. CONCLUSIONS

Chemical analysis of water samples collected from geothermal wells: 4003, 4011, 4012 and Balint from Băile Felix indicated that these waters present a high bicarbonate content and calcium is the most dominant cation. It was also noticed a high sulphate content, at Balint well being recorded the highest value. The silica concentration is moderate, a little higher at Balint.

A low pH, the presence of chloride and of dissolved oxygen into the geothermal water represent factors which affect the exploitation equipments by stimulating the corrosion processes. The electrochemical corrosion was studied in the chemical laboratories of the University of Oradea. After gravimetric research in static conditions it can be concluded that the most corrosive tendency present geothermal water from well 4011. The analysis were done at temperature of 40ºC, which is the wellhead temperature of the wells taken in this work and at 25ºC, temperature that can be reached by utilization. Corrosion is more pronounced at the beginning of the exposed period. Then the corrosion rate tends to establish to a value with one order smaller. At the production temperature, 40ºC, corrosion is higher. It was observed a uniform corrosion and after about a month a pitting corrosion becomes. For geothermal waters from well 4011 the corrosion rate was measured in dynamic conditions as well, obtaining a double value compared to static conditions. It was considered the anti-corrosive protection with additives. There were made experiments with a precipitation additive, disodic phosphate and an adsorptive additive, tiouree.

It was recorded the better efficiency of disodic phosphate additive. Even at a 25 ppm dosage it reduces significantly the corrosion rate of the coupons. It was verified at production temperature for waters from wells 4003 and 4011. In both cases it was proved the efficiency of the used anti-corrosion additives, being recorded a protection efficacy between 50 – 70% for disodic phosphate at a concentration of 25 mg/l and its efficiency becomes more than 90% at dosages of 100 ppm.

Being easier to prevent a problem than to fix it after it happened, it was simulated the mineral deposition which can precipitate from the geothermal water. A solid sample collected from the pipes of the well 4003 was structural analysed The X-Ray diffraction analysis indicated calcite as main component of the solid deposit and quartz, as it was assessed by the simulation program.

In laboratory conditions, by using an installation which allows measuring the pressure, in a capillary tube, as the precipitation takes place, were performed tests with anti-scaling additives. It was proven the better efficiency of the phosphate additive.

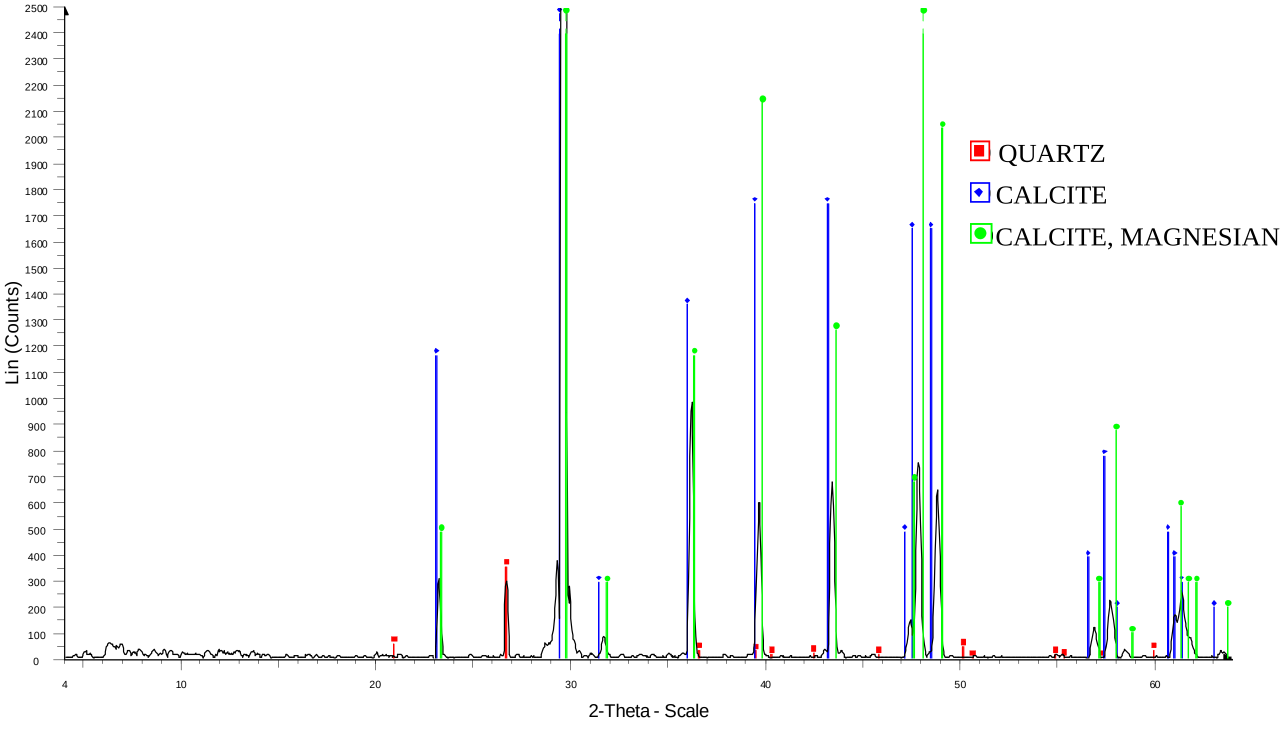

Figure 7: The XRD diagram for solid deposition.

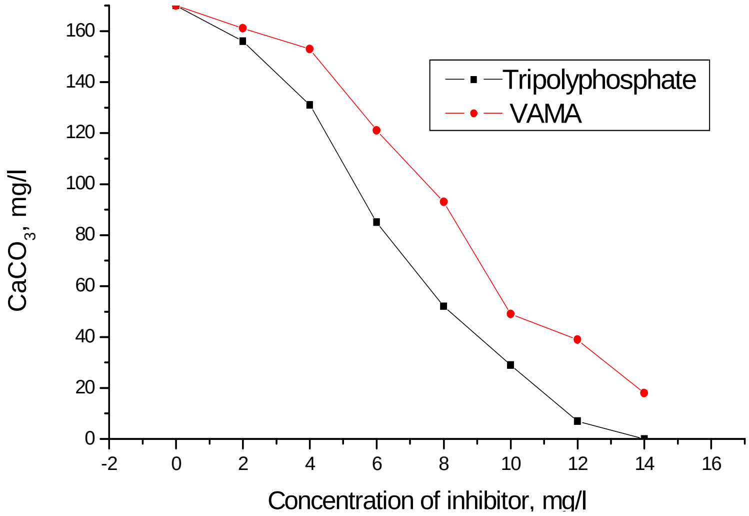

Figure 8: Deposition control.

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