The Study of Carbon Steels Corrosion in Geothermal Systems of Lower Enthalpy

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The physico –chemical and thermodynamic properties of the geothermal waters create a series of problems when they are exploited. The most common lacks are due to the corrosion which is initiated and maintained by the diluted gases. This research has as its main purpose to establish the influence of the physico-chemical characteristics of the geothermal fluid upon the mechanism and the corrosion speed of carbon steels, used to obtain pipes which transport thermal water. In order to determine the corrosion behaviour of metal materials which have contact with thermal waters, we determined the corrosion speed of four types of carbon steels and identified the depolarizers through the study of corrosion products.

Keywords: physico-chemical properties, corrosion, depolarizer species

The geothermal energy is used today in more than 60 countries around the world, in order to produce electrical energy or for other direct energy applications. Taking into consideration the energy they contain, the thermal waters from Bihor county, about whose existence we have written documents since 1221, they are part of low enthalpy deposits (the temperature at a 1000 meters depth is not more than 150°C).The existence of important thermal water deposits in the north-west part of Romania facilitates the use of this energy form on the local area, for different purposes, ensuring the saving of a quantity of conventional fuels.

The physico–chemical and geothermal properties of geothermal waters create a series of problems when exploited. The most common lacks are due to the corrosion which is initiated and maintained by the dissolved gases: carbon dioxide, sulphuretted hydrogen, oxygen and to the sediments caused by the presence of the bicarbonate, sulphate, sulphides, silica. The important factors which generate the two phenomena are: the pH number, gas solubility, their partial pressure, water mineralisation, solubility of the formed products at the change of thermodynamic conditions induced in the usage process. In some cases the sediments obstruct the corrosion or on the contrary, the corrosion creates active centres where the sediment of insoluble substances starts [1-3]. There are also many situations in which the sediments promote the corrosion by modifying the potential of different regions of the metal surface [4,5].

The technical problems the users have to deal with are specific because the chemical characteristics of geothermal waters vary from one collector to another. Moreover, different problems can be identified in different parts of the same equipment. The thermal waters from Bihor county contain, in the liquid phase, ions and substances such as: bicarbonates, sulphates, chlorinates, calcium, magnesium, sodium, potassium, sometimes ammonium, iron, silicon dioxide, phenols. The dissolved gases are usually: carbon dioxide, methane and sulphuretted hydrogen. The oxygen often appears and this is usually due to the exercise done during the usage.

Experimental part

It is known the fact that the carbon steels corrode in the geothermal mediums, sometimes with speeds which make them uneconomical. This type of steels remains the most used material for the geothermal domain even if it has another disadvantage: the pipes corrode in the external side too especially when buried in wet soils.

In order to achieve the target purposes, the study of the waters from the two important collectors in the north-west of Romania, has been considered as being opportune: Panonian and Triasic, because the waters have different compositions. The researched pipes within the same collector have been chosen according to the information about the effective behaviour of the waters, i.e. their tendency to form rims or to corrode the metal materials. There have been chosen only the pipes which have a few sediments, knowing the fact that the two effects are, at least at a certain moment, antagonistic. The choice of the well 4797 Dublet Oradea has been done in order to solve the problems which occurred during its functioning and the well 3001 Beius in order to monitor the features of the new drilling, for a better knowledge. The well 4691 Sacuieni has been chosen because it is interesting due to the fact that the thermal water deposit is accompanied by significant quantities of sulphuretted hydrogen, which is supposed to be involved in the corrosion process.

The metallic materials which are studied have been chosen taking into consideration the frequency they are used for the construction of the thermal waters transport equipment. These are: OLT 35 K, OLT 45 K, OLT 35 R , OLT 45 R .

In order to get accurate results, a physico-chemical study has been considered necessary for each of the three wells, at the very beginning of the experiments. The important anions and cations which define the character of the water have been determined and also the diluted gases: oxygen, carbon dioxide and sulphuretted hydrogen have been determined and settled there, on the spot and after that they have been studied. The results of these tests for the three wells are presented in the table 1.

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Table 1
VALUES OF THE MAIN INDEXES OF WATER DETERMINED DURING THE EXPERIMENT

Main indexes	M.U.	Well 4797 Dublet	Well 3001	Well 4691
pH	unit.	7.2	6.5	7.1
CO_3^{2-}	mg/L	153.80	209.9	731.52
Cl^-	mg/L	10.30	15.21	2410.20
SO_4^{2-}	mg/L	664.60	47.00	35.19
Ca^{2+}	mg/L	296.60	65.50	71.89
Mg^{2+}	mg/L	21.90	12.22	23.09
Complete S^{2-}	mg/L	2.31	1.74	5.5
H_2S	mg/L	0.55	0.97	1.6
Diluted O_2	mg/L	3.39	2.09	absent
Free CO_2	mg/L	7.29	11.25	28.53

We have chosen the method of testing in working equipment in order to determine the behaviour at corrosion of the metal materials which have contact with thermal waters in the transport and stocking equipment [6]. This has been preferred to the lab simulation methods because the geothermal fluid changes its characteristics very much once the system becomes, inevitably, open .The water transported in the lab differs due to the direct parameters involved upon the corrosive or embedded action. The quantitative method chosen was that of mass loss because it offers quite accurate results and the soil conditions don't allow the use of electrochemical methods which involve the use of electronic equipment. The corrosion speed has been measured with the help of the gravimetrical and penetration index. The test bars used during the experiment have a ring shape. They have been cut off from steel pipes, unprotected, without weld, done at cold. The tests which are subject to corrosion have the following dimensions: external diameter = 20 mm, wall thickness = 2 mm, rings length = 10 mm. There have been made 36 rings, 12 for each type of steel. They have been placed, for each well, on three transoms, so that they can be extracted from the plant at different time limits. The chosen time limits have been 30, 60 and 90 days. In order to identify the depolarizers from the corrosion process, the collected products from the metal test bars have been subject to many kinds of analysis. The chemical products deposited on transom II have been subject to a physico- chemical study which had as a main purpose to identify some anions and cations supposed to be present and to determine their concentration in the tested material. The study of a single test, always chosen from transom II, for all the three wells, has been considered enough. The physico-chemical analysis has consisted of volumetric, spectrophotometric and atomic absorption spectrometry. In order to get a better identification there have been done X-ray diffraction analysis and thermo-gravimetrical analysis too. The X-ray analysis has been done on the Diffractionmeter DRON -3. The diffraction has been done using the copper radiation (λ = 1.54 A), with a nickel filter.

Well 4797Dublet. A test, weighing 580 mg, has been collected by rubbing off with a plastic brush in order to be analysed. Taking into consideration the chemical composition of the water and the aspect of the corrosion products, which seemed to indicate a majority composition of steel oxides, we intended to dose the carbonate, sulphate, sulphides, iron, calcium and magnesium.

The determination equipment was a barbotage vessel train, having the argon as a carrying gas. The sulphides and carbonates have been soluble by treating them with hydrochloric acid 1: 3. The sulphuretted hydrogen has been retained by treating it with zinc acetate, and the carbon dioxide has been retained in a solution of barium hydroxide of 0.15%. The content of the barbotage, which contains the zinc acetate, has been titrated directly with a solution of iodine N/1000, in the presence of starch. The sulphuretted hydrogen is not present in the test more than the detection limit of the method. The carbon dioxide quantity has been determined in the next barbotage. The rest of the solution, after taking over the carbon dioxide, has been restarted at heat with nitrogen acid 1:1, filtered, after that the calcium, magnesium and iron have been dosed by atomic mass spectroscopy. The sulphate has been determined through the turbidimetric method. The rest from the filtration has been dried, baked in a platinum box and treated with acid in order to determine the silica dioxide.

Well 3001. The sediments removed from the rings of the second transom have been subject to the physico-chemical study. The rim has been removed from the rings by scraping with a plastic brush. The total amount of the rim was 56.2 mg. This amount of the rim has been transferred into a determination system for sulphides and carbonates made up of a phial which contains 20 mL hydrochloric acid 0.2 n, followed by two reaction balloons with a volume of 100 mL. In the barbotage vessel with 10 mL cadmium chloride is introduced, with a concentration of 0.5% acidulated at *p*H number 3, with hydrochloric acid. After assemblage, carbon dioxide circulates through the system in order to remove the air then the content of the acid phial is transferred into the reaction balloon. The reaction period is of 30 min and after that, the amount of the resulted sulphide is determined. The titrant is the iodine solution N\1000, and the colour indicator is the starch. The addition of the iodine solution is of 100, added from a piston biuret, directly into the barbotage vessel.

Well 4691. The sediments collected from transom II have been subject to a physico-chemical study. The tested amount has been 376.7mg. For the study, an installation has been done, formed of a barbotage vessel with hydrochloric acid, a reaction vessel with test, a barbotage vessel with cadmium chlorinate, solution 1% and reaction vessel with barium hydroxide. An argon current ran through these vessels, with a flow of 50 mL/min. After the air disposal, the acid has been transferred into the test vessel. The barbotage continued until the sulphide hydrogen recess finished. The amount of cadmium sulphide has been measured by direct titration with a solution of iodine 0.01n. The partially diluted test has been subject to a treatment with concentrated nitric acid. The iron, calcium and magnesium have been measured by atomic absorption, after an appropriate dilution. The sulphate content has been measured after the turbidimetrical principle.

Results and discussions

The results of physico-chemical analysis of the products on the test bars for the three wells are presented in the table 2.

For the well 4797 Dublet, the chemical study shows the majority presence of iron, representing 60.34% of the analysed test. Other present cations are those of calcium and magnesium. Their setting is done under the form of sulphates and carbonates. The majority compounds of the iron seem to be the oxyhydroxides like Fe OOH x nH_2O. It

Tabelul 2
THE RIMS COMPOSITION
DETERMINED THROUGH
PHYSICO - CHEMICAL STUDY

Indicator	Well 4797 Dublet		Well 3001		Well 4691	
	Quantity (mg)	% mass	Quantity (mg)	% mass	Quantity (mg)	% mass
$Fe_{tot.}$	350.00	60.34	22.00	39.15	144.25	38.30
Ca^{2+}	26.00	4.48	5.60	9.90	12.01	3.18
Mg^{2+}	3.00	0.52	0.46	0.81	1.95	0.52
CO_3^{2-}	8.18	1.41	4.03	7.17	90.22	23.95
SO_4^{2-}	7.00	1.20	-	-	20.60	5.46
S^{2-}	-	-	0.40	0.71	2.34	0.62
SiO_2	70.00	12.07	-	-	-	-
Total	464.18	80.02	32.49	57.74	271.37	72.03

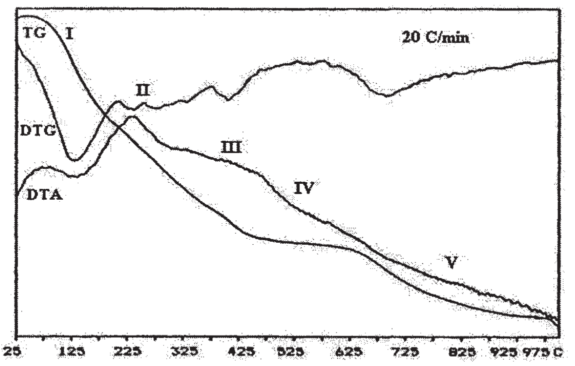


Fig. 1. The diagram of the thermo-gravimetrical analysis for the products of the well 4797

is also noticed the setting of SiO_2 in the rim, from the impurities which accompany the water.

The comparative study of the water and rim shows that the sulphates can be found together with the carbonates, a strongly oxidative process of the iron from the test bars being also encountered, mainly caused by the diluted oxygen from the water. The percentage difference up to 100% for the study of the sediment is represented by the water from crystal-hydrates and the oxygen caught in the oxyhydroxides. The thermal differential analysis shows the presence of an exothermal effect and of a little mass loss on the 125-475°C temperature range, which may be due to some organic substances from the water, absorbed in the rim.

The thermogravimetrical analysis diagram presented in figure 1 shows a mass loss of 15.58% during the transformations.

The diagram can be divided in five areas: on the first part we consider that there is a process of water drying and elimination, possibly from the hydrated oxyhydroxides of the iron. On the second part there is an exothermal process, maybe of splitting/resolution of some organic substances and also a process of crystallization water loss. The third section contains the splitting of organic substances and water loss from crystal-hydrates. The last one section is an intermediate area between the splitting of crystal-hydrates and calcium and magnesium carbohydrates. The splitting of the possible iron carbonate takes place on this section. The last transformation is that of magnesium and calcium carbonates splitting, which starts at 625°C and finishes at about 900°C.

The X-ray analysis shows, on the first place, the high degree of amorphization of the chemical compounds from the rim. This can be explained through the low formation temperatures and the low age of the rim. The only identified crystallized form is the phase Fe_2O_3 resulted from the iron oxidation process from the metal material of the test bar. For a better understanding the test has been burnt at 1000°C and slowly cooled according to the free cooling curve of the oven. This operation followed by a new X-ray diffraction analysis confirms the majority presence of the compounds like FeOOH hydrates in the test. These are transformed in Fe_2O_3 after burning, regardless the crystal-chemical form they exist in the test. The possible calcium and magnesium oxides resulted from the burn of the carbonates can not be found on the RX diagram because of their low concentration in the test and because, by burning at this temperature, it is possible that the crystallization degree could not make them obvious with the apparatus it has been worked with. In figure 2a the X-ray diffraction analysis of the unburnt test is presented and figure 2b shows the X-ray diffraction analysis of the burnt test up to 1000°C.

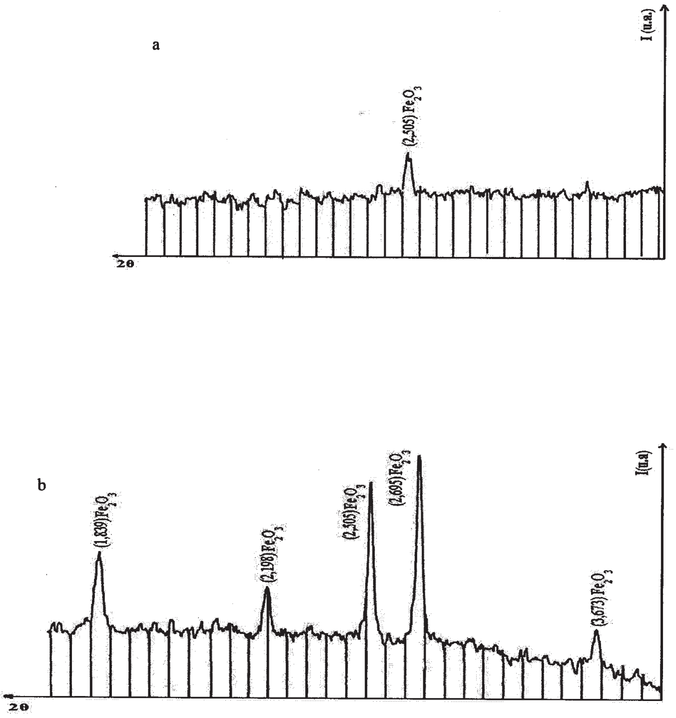


Fig. 2. The X-ray diagram for well 4797
a-unburnt test; b-burnt test

For the well 3001, due to the fact that the rim has been removed only partially, the four rings have been introduced into the reaction balloon and the same procedures to determine the iron and calcium sulphides have been followed. It is obvious that the values obtained for the iron in this case include the diluted iron from the metal ring. The result of the study is the following: sulphide-0.43 mg, calcium-2.04 mg, iron-225 mg.

It seems that the deposited products on the test bar contain quantities of carbonate and probably calcium sulphate. The sulphides content is little and they are found in a larger amount on the ring not on the rim. This seems to suggest an attack of the metal from the sulphuretted hydrogen, followed by the covering with a layer of iron, carbonate sulphides and calcium sulphate. It is obvious that the iron amount comes from corrosion as it is also shown by the loss of weight of the test bars .The so formed compounds layer is compact and adherent enough to behave like a barrier which prevents the oxidation and reduction processes. The iron ions react with the acid sulphide ion either in solution or on the surface of the corroded metal, forming iron sulphides, usually amorphous. Their chemical formulae are most of the time like: $Fe_{1-x}S_x$. The sediments can be considered as having two layers: the layer next to the metal is formed of the most soluble substances, like: FeO(OH), $Fe(OH)_n$, $FeCl_2$, and the layer next to the solution is formed of the most insoluble substances: iron sulphides. The sulphides are formed at the beginning, which are deposited at the interface solution/metal (pK_sFeS = 17.7). The anions from the water can diffuse through the sulphide layer, from the solution to the metal and the iron ions powered by the corrosion process, from the metal to the solution [7]. When the iron ions have contact with the anions, some insoluble substances result which are formed in the reversed order of the solubility of the mineral species, probably starting with the iron carbonate (pK_sFeCO_3 = 10.45). The calcium and magnesium ions are fixed as carbonates [8].

The physico-chemical study shows the majority presence of the iron ion, as a result of the corrosion process, followed by the calcium and carbonate ions. The percentages which can not be found after the study may be due to an amount of hydrated compounds like iron oxyhydroxides or iron oxides.

The diagram resulted from the thermo-gravimetrical analysis of the sediments (fig. 3) revealed a mass loss of 36.66% during the transformations. These transformations consist of drying and water loss from crystal-hydrates, for the first part of the diagram, and carbonates splitting in the phase III. The intermediate phase does not reveal changes of the tested mass.

The X-ray test, shown in figure 4 confirms the presence of magnesium and calcium carbonate with line d=3.03 A, d=2.06 A and d=1.89 A, and also of the iron oxides.

For the well 4691 the derivatographic study of the test presented in figure 5 shows:

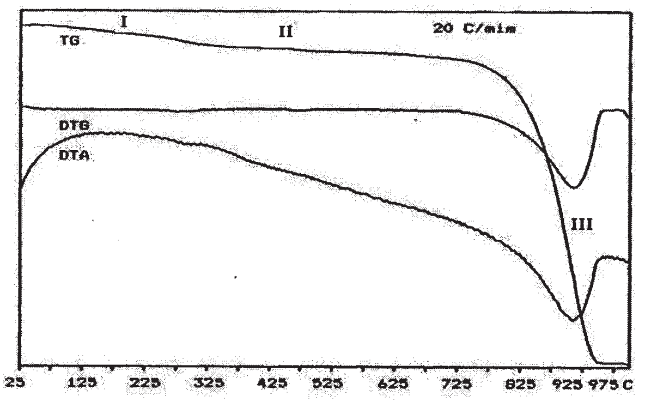


Fig. 3. The diagram of the thermo-gravimetrical analysis for the products of the well 3001

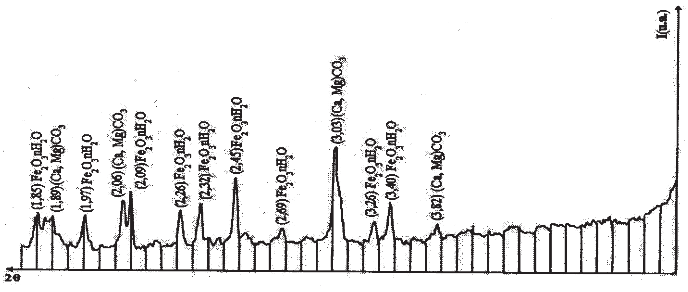


Fig. 4. The X-ray diagram, well 3001

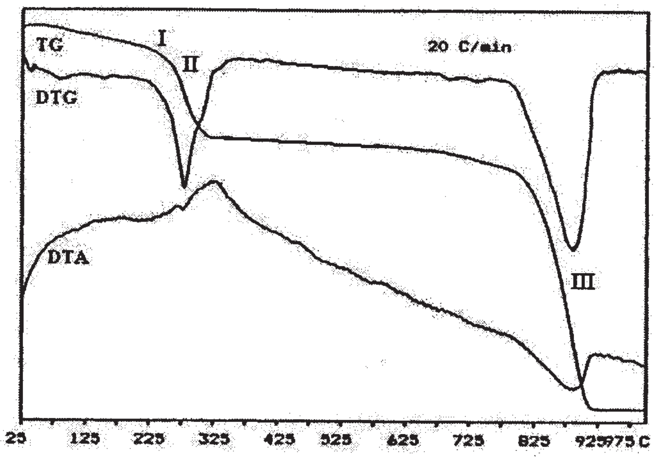


Fig. 5. The diagram of the thermo-gravimetrical analysis for the products of the well 4691

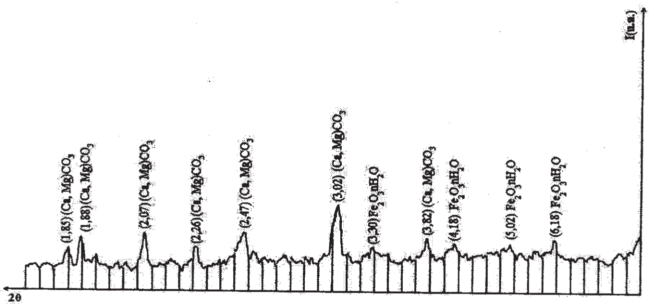
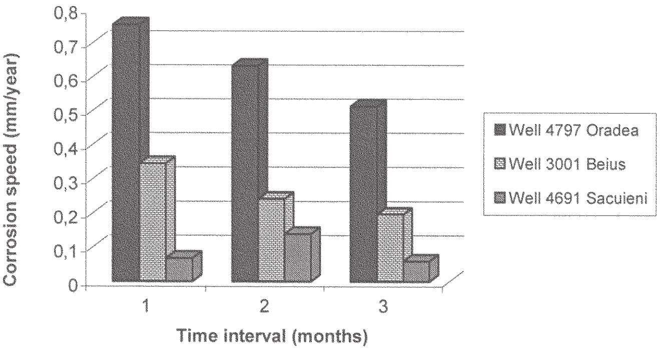


Fig. 6. The x-ray diagram, well 4691



Fi. 7. The variation of the corrosion speed for the three afferent studied wells OLT 35K

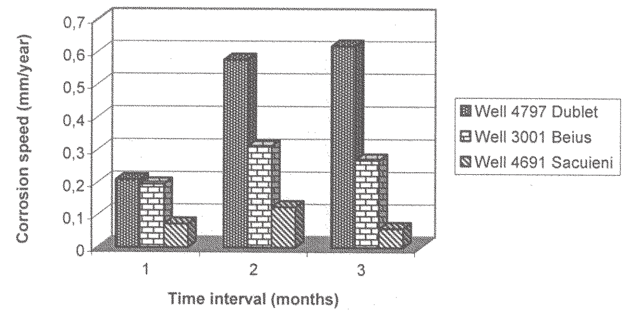


Fig. 8. The variation of the corrosion speed for the three afferent studied wells OLT 35R

I - on the temperature interval between 200-325 °C an endothermal splitting process has been noticed which corresponds with the water disposal which is chemically connected from phase $Fe_2O_3.nH_2O$;

II – an exothermal process which starts at about 250°C and continues up to 350°C can be due to the oxidation of organic substances which accompany the tests and the deposit;

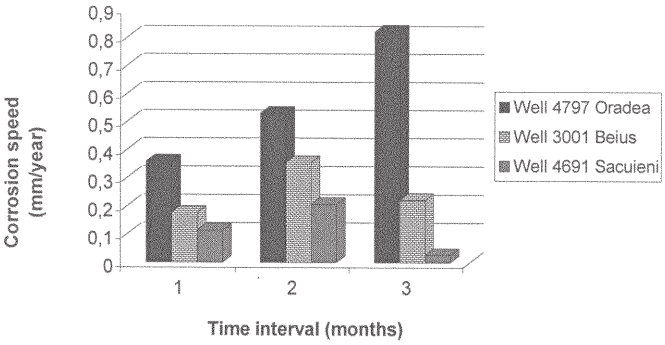


Fig. 9. The variation of the corrosion speed for the three afferent studied wells OLT 45K

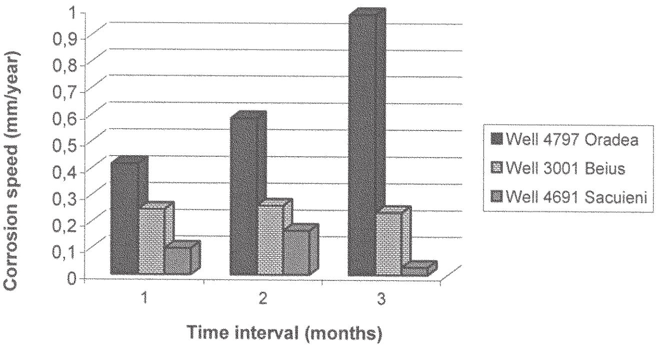


Fig. 10. The variation of the corrosion speed for the three afferent studied wells OLT 45 R

III – a strong splitting process which starts at about 800°C and finishes at about 925°C, due to the splitting of calcium and magnesium carbohydrates.

The X-ray experiment done on the test and presented in figure 6 shows the majority presence of calcium and magnesium carbonate and also of a complex phasal composition like $Fe_2O_3.nH_2O$.

As regarding the variation of the corrosion speed we have noticed that, for all the four tested types, the highest corrosion speeds are encountered in the case of the fluid of the well 4797 Oradea (diagrams 7 - 10,). The corrosion speed in the case of OLT steel 45 R, after 101 days of immersion, surpasses the value of 0.9 mm/year, over which, according to the decimal degree scale of corrosion resistance, the steels are considered as being little stable. It is possible that this value be surpassed together with the increase of the immersion time because, during the experiment, the corrosion speed increased constantly in the case of this fluid (except OLT35K steel).

The lowest corrosion speeds, for all types of steel, have been encountered at the fluid of the well 4691 Sacuieni.

Conclusions

Taking into consideration the results of the experiments, we can conclude that the most aggressive species to initiate corrosion is the oxygen, which is reduced in the geothermal medium at O_2, at the same time with the iron ionization at iron ion. This is found at the highest concentration (3.39 mg/L) at Oradea well and it is absent at Sacuieni well. In the case of the last well, the presence of the sulphuretted hydrogen is not very aggressive for the metallic wall, as long as the gas is kept in the solution. At all the water exits from installations, when the sulphide hydrogen is degasified, the corrosion is stronger and it can be seen on the ground. The large amount of carbon dioxide diluted in the water of the same drilling seems to be under that of balance, considering the large amount of bicarbonates.

After the start of the corrosion, the nature of the products deposited on the metal surfaces has an important role regarding the speed of the process. The information we had previously has been confirmed by the results of the physico-chemical studies done within the experiment. The majority of the chemical combinations present in the products deposited on the test bars is not given by the carbonate or calcium or magnesium sulphate, but by the iron compounds, like oxides and oxyhydroxides, or by the sulphides, part of them being oxidized during the process of test bars drying, at sulphate. The experimental data show that the layer of the products deposited on the immersed test bars in the water from well 4797 Oradea doesn't ensure the protection of the metallic wall. The products, in a large amount, are quite porous, so that on the covered areas the reaction of iron oxidation still happens and on those areas where there is a quite good water access, the reduction reactions take place. The potential difference between the free and covered areas is an engine which maintains the corrosion. The fact that the products have a porous structure encourages their release from the metal walls as a result of the fluid flow. These aspects are sustained by the constant increase of the corrosion speed for the drilling water. In the case of the wells from Beius and Sacuieni, the deposited products are much less. Their presence is good for the isolation of the metal wall against the aggressive species. Most of the sediments are formed of iron sulphides, amorphous or even crystals. They have the aspect of a compact, good insulator, adhesive film and the corrosion speeds decrease in time after two months from the immersion.

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