OVERVIEW OF THE DEPOSITION PHENOMENA IN GEOTHERMAL WELLS IN THE PARIS BASIN

Mohamed Amalhay, **Afif Abou** Akar and Ioannis Ignatiadis

BRGM, Research Division, Department of Geotechnical Engineering and Mineral Technology,
Avenue de Concyr, BP 6009, 45060 ORLEANS, (France).

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ABSTRACT

In geothermal installations exploiting the Dogger aquifer in the Paris Basin, field esperience has shown that corrosion in production and injection well casings made of carbon steel occurs mainly because of the available compounds which confer a high potential for corrosion relative to the well casings. The relatively high fluid temperature (T: 43° to 85°C), total dissolved salts *(5* to 35 g/l), and the presence of Cl^-H_2S/HS^- and CO_2/HCO_3^- make them one of the most corrosive naturally occurring fluids known.

The corrosivity of various geothermal fluids was assessed with respect to different materials, including carbon steel, under different operating conditions (flow rate, fluid temperature, treatment by corrosion inhibitor). Both weight loss and electrochemical methods were used to measure corrosion rates. The scale produced under these conditions was characterized by classical chemical analysis, X-ray diffractometry (XRD), metallography, scanning electron microscopy (SEM) and electron dispersion spectroscopy (EDS).

These experiments show that carbon steel samples suffer fairly general corrosion. The corrosion rate and scale thickness are decreasing functions of the flowate of the fluid. Mineralogical analysis shows that the scale is composed mainly of iron sulphides (mackinawite, pyrrhotite, pyrite, greigite, marcasite), calcite, siderite, and iron hydroxide and hydroxychloride and that the S/Fe ratio in the scale increases as a function of exposure time. The nature, distribution and abundance of these phases is a function of the nature of the metal substrate upon which they have formed, of certain physicochemical parameters of the fluid, of the origin of the scale (depth) and of the operating conditions. These results, together with those from the study of the formation conditions of the various phases, has made it possible to explain the origin, the on site formation conditions and the relative abundance of the different phases. Mackinawite, pyrrhotite, greigite, siderite, and iron hydroxides and hydroxychlorides are products of casing corrosion, whereas pyrite, silica, quartz and marcasite come mainly from the reservoir in the form of euhedral micrometer-sized particles. The origin of the iron (from both the reservoir and corrosion) and of the dissolved sulphides (from both the reservoir and current bacterial activity), and the influence of these species on scaling processes are discussed. **A** model of scaling regulation (control) is proposed, suggesting that the formation of scale is controlled by the diffusion of anions (sulphide, hydrocarbonate, chloride) through the scale.

1. INTRODUCTION

Scaling has often been identified as a source of problems in the production of large flow rates from drill holes, especially in the development of the oil and geothermal industries.

The Dogger aquifer in the Paris Basin is a well characterised low enthalpy resource in a sedimentary environment. From core samples obtained during drilling, the matrix has been described in several places (Kojas *et al.,* 1989). In general, it is made up of very porous carbonated rock. The cavities are, in some places, lined with euhedral pyrite, in places taking the form ofveinlets, in places large carbonate crystals and in rare cases secondary clay minerals. The zonation is marked by porosity. The pyrite cavities could be a result of fluid inclusions or, more likely, cavities left by dissolved mineral phases other than pyrite Fluid inclusions are observed in the newly formed carbonates. No other sulphide (in particular, iron sulphide) except for rare traces of marcasite in the pyrite, was found, nor is there any trace of metal sulphates (Rojas *et al.,* 1989).

The geothermal fluids of the Dogger aquifer form an anaerobic media characterised mainly by the presence of Cl^- (0.073 - 0.564 M), H_2S/HS^- (0 - 3 mM), SO_4^{2-} (0.025 - 0.125 M) and CO_2/HCO_3^- (3 - 5 mM). The total dissolved salt content, pH and temperature range from 6 to *35* mg/l (ionic strength, 0.1-0.6 M). 6.1 to 6.7 and 43 to 85°C, respectively These fluids flow unassisted or assisted through the carbon steel casings to the surface and are reinjected into the formation after flowing through heat-exchangers. Problems related to scaling have been signalled by the modification of hydrodynamic properties in wells (increase in re injection pressure, decrease in production pressure). For the last four years, some of these fluids have been treated against corrosion with an organic corrosion inhibitor of the quaternary ammonium salt type (Ignatiadis *et al.,* 1990).

Chemistry, isotope and gas studies (Fouillac *et al.,* 1990; Criaud *et al.,* 1988a; Marty *et al.,* 1988) have revealed distinct zones corresponding to various degrees of iron sulphide scaling. In particular, investigations into the chemical composition of the fluids of the Dogger showed a marked variation in dissolved sulphide (Ignatiadis *et al.,* 1990, 1991, 1994). Zones of maximum sulphide concentration coincided with the site locations at which clogging had occurred (Fouillac *et al.,* 1989, 1990). The decrease in the hydraulic diameters of the casings of both production and injection wells occurred mainly in the Seine-Saint-Denis department (north of Paris) where the highest sulphide contents were measured.

While the major scale layers have been identified (Amalhay *et al.,* 1994), progress remains to be made in determining the precise origin of the scale phases and the mechanisms of formation, control and evolution as a function of operating and physico-chemical parameters. In order to provide answers to these questions, the scale which has been deposited during as much as ten years of exploitation has been examined. The results of chemical and mineralogical analyses of scale, in particular on well casing at different depths, but also on heat-exchangers, corrosion coupons and the wellhead filters have been studied and allow us to explain the origin, the conditions of formation on site and the relative abundance of the different phases.

2. RESULTS

The scale that has been deposited during as much as ten years of exploitation was obtained 1) on the wellhead filters (0 01 μm to 500 μm in size), 2) on heat-exchangers (titanium), 3) on coupons of carbon steel or of uncorrodable materials placed in pipes at the wellhead before and after treatment by corrosion inhibitor, and **4)** on well casings at different depths (before treatment) from rehabilitated production and injection wells

These scale samples were studied using optical microscopy, XRD, SEM, EDS and scanning transmission electron microscopy (STEM) Chemical methods for analysis of solids and liquids were also used

2.1. Scale obtained on the wellhead filters

For non-treated fluids, the suspended particles obtained by filtration at the well head of the production well represent up to several mg of solid matter per litter of fluid (Ignatiadis *et al.,* 1992) This solid matter generally contains an amorphous part of iron sulphide and a crystallised part made up chiefly of pyrite. Amorphous iron sulphide, mackinawite, pyrrhotite, greigite, calcite and siderite are occasionally present in variable proportions. Traces of marcasite, quartz, elemental sulphur, hematite, magnetite, geothite, lepidocrocite, akaganeite, smectite, feldspath, kaolinite and illite are sometimes found. When fluids are treated with a corrosion inhibitor, the particles obtained by filtration are, for the most part, made up of pyrite. Marcassite and occasionally mackinawite, calcite and siderite are also found. It should be noted that there is no iron oxide nor iron hydroxide.

2.2. Scale formed at the surface of titanium heat exchangers

Scale recuperated from the titanium of the heat-exchangers *is* similar to that retained by the filters except that there is even more pyrite. Iron sulphide (such as amorphous FeS, mackinawite. pyrrhotite, marcasite and greigite), calcite, siderite and magnetite are occasionally found, as are traces of quartz. elemental sulphur. hematite, magnetite, geothite, lepidocrocite, akaganeite. smectite, feldspath, kaolinite and illite.

2.3. Scale formed at the surface of carbon steel samples

Scale formed at the surface of carbon steel samples withdrawn from the geothermal fluid after various lengths of exposure time consists of two main layers (Amalhay *et al.*, 1994).

a) The first layer adheres to the metal as a thin layer composed mainly of iron oxide (Fe_xO_y), oxy-hydroxide (α-FeOOH goethite and γ-FeOOH lepidocrocite) and hydrated hydroxides $Fe(OH)_n$, iron hydroxy-chloride and small lumps mackinawite, magnetite, siderite (Fig. 1, 2, 3, 4).

b) The second, generally thicker, layer, which is easily detached, consists of a mixture of iron sulphides, siderite and calcite (Fig 1. 2, 3, 4). Mineralogical analysis showed that this layer is composed of more than 70% iron sulphides (mainly as mackinawite, greigite, pyrite and pyrrhotite). Siderite, lepidocrocite, goethite, sulphur, calcite and occasionally magnetite are sometimes present, but are always in minor amounts.

Nevertheless, other configurations are found, depending on the sulphide concentration in the fluid. Indeed, the thicknesses of the two layers can van, in such a way that it becomes impossible to distinguish the layer of hydroxides when the sulphides are abundant (>40 mg/l). When the sulphide concentration in the fluid is very low (<3 mg/l), only the first layer *is* present and most often in the form of small pill of hydroxides distributed on the surface of the metal while the corrosion appears to be uniform

Mackinawite is sometimes in competition with iron hydroxide in the first layer This appears to be a progressive replacement of FeOOH by mackinawite as the HS^- reaches this layer and passes through the porosity of the scale The FeOOH/Fe_xS_y layers are sometimes alternated (Figs. 4, 5). When there is pitting. the pocket *is* filled with iron hydroxide and covered with a deposit of iron hydroxide, itself covered with iron sulphide (Fig. 6).

Analysis of the scale at various exposure time shows that the S/Fe ratio increases as a function of exposure time. Although ven, few sulphate reducing bacteria (SRB) are present in the circulating fluid. they are found in much greater and variable numbers on the coupons (from several bacteria/cm^2 to several million/cm^2). Enormous differences were found in the number of bacteria counted on the carbon steel surface and on the stainless steel or titanium surface exposed for the same length of time This shows that the number of bacteria is linked to the presence of a thick scale. Indeed, examination of polished sections with a metallographic microscope revealed that the mackinawite actually formed within the bacterial skeletons (Abou Akar and Lafforgue, 1994)

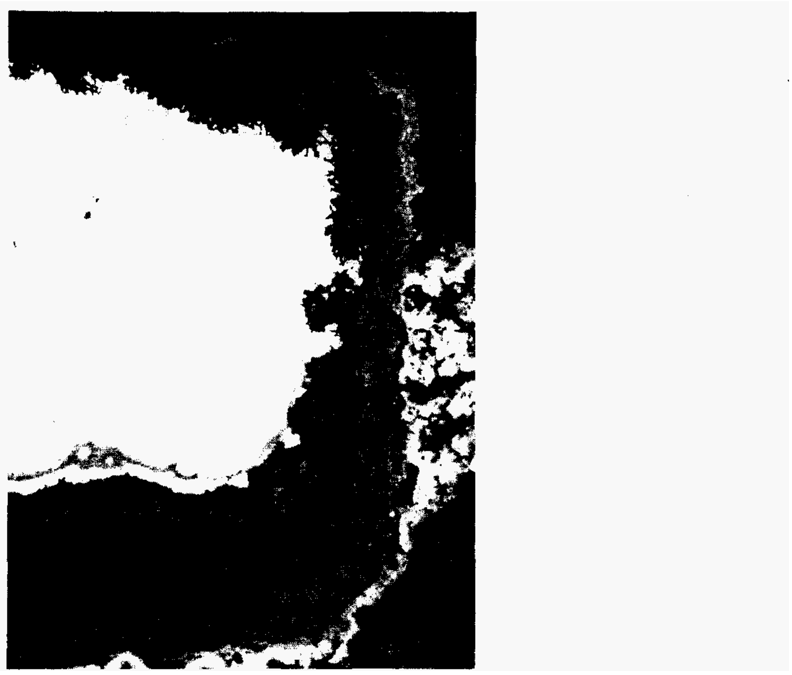

Fig. 1. Carbon steel section surrounded by corrosion products, iron hydroxides and oxyhydroxides, having maintained the initial form of the section These substances are overlain by an irregular deposit of iron sulphide which is detached along a straight line (x 30)

Fig. 2. Significant growth of pyrrhotite on goethite (α-FeOOH). Presence of SiO_2 and FeOOH with pyrrhotite. Note the existence of a very straight separation line Growth of pyrrhotite on geothite, presence of a pyrite grain (x 120)

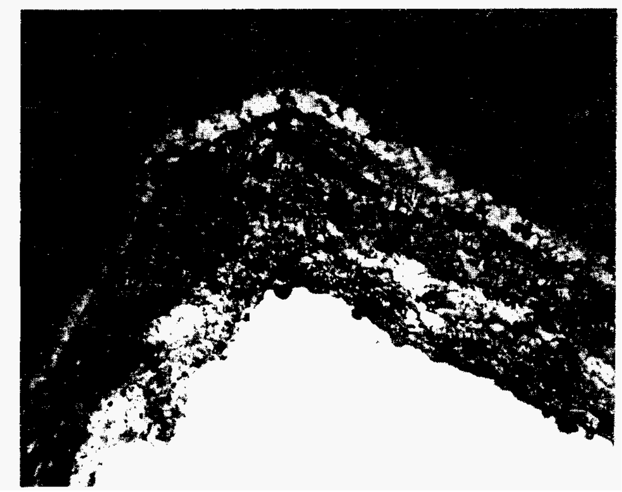

Fig 3 View ot the corner of a coupon and the successive layers that overlie one another steel goethite mackinawite in a silica rich matrix (90 %) goethite and small grains of carbonate (x 60)

Fig 4 View schowing alternance **of** FeOOH/FeS traces of mackinawite surrounded by goethite, thick laver of iron sulphides (pyrrhotite) in equilibrium with FeOOH and external laver of pyrrhotite with a dendritic structure (x 120)

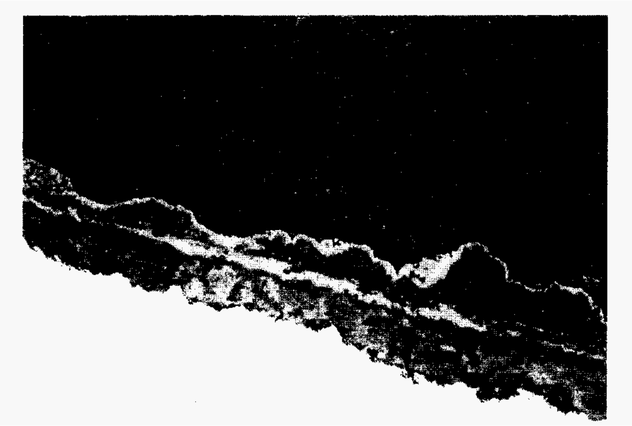

Fig 5 Section showing alternating oxides / sulphides / oxides sulphides (x 120)

Fig. **6** Section displaying local corrosion, pockets are filled with iron oxides and covered by a scale of iron sulphides The iron sulphide scale is made up essentially of fine pyrrhotite. Note that mackinawite is present in the pockets of iron oxides (x 120).

2.4. Scale obtsined from different depths

The depth of the origin of the scale is esiimated with a precision of 50 in. The scale particles rise to the surface with ihe water injected during cleaning Knowing the depth of the cleaning apparatus. we can deduce the depth of the origin of the scale.

'The nature of the scale is sometimes more or less clearly linked to the depth ieffect of pressure), to the type of well (producion or injection), to the physico-chemistry of the fluid (T. pH, Eh, ionic strength), and to the hydraulic regime (operating discharge rate).

All samples obtained from different depths and different wells occasionally have discontinuous layers of different phases of iron sulphide, the alternance of these sulphides not being homogeneous Analyses by XRD. SEM or metallography revealed the presence of large amount (> 70%) *of* iron sulphide, whatever the role of the well. Mackinawite is the most abundant, followed by pyrite, pyrrhotite and greigite. Pyrite **is** more often found at the bottom of the production well than elsewhere and is most often in the form of automorphous crystals formed elsewhere and transported by the fluid, but it sometimes has a cryptocrystaline structure in places. We can observe minor amounts of iron hydroxide and hydroxy-chloride (***5*** to 10 %), siderite and calcite (10 %). Calcite is most often found in samples taken at the bottom of wells but occasionally appears at higher levels. Marcasite and greigite were also reported. Pyrite and greigite are generally found together and are cemented by calcite. iron hydroxide and, in small quantities by iron carbonate. Trace metal analysis reveals the presence of heavy metals (Cr. Mn, Ni, Cu, **As,** and Mo) in the iron sulphide phases, but they do not form true sulphide minerals. There is no amorphous iron sulphide in the scale studied.

The percentage of doininant mineral species in the scale varies with the depth of sampling and the role of the well (production or injection). In the production wells, the shallower the depth, the higher the percentage of mackinawite in relation to pyrite and pyrrhotite. In particles gathered at the end of the scouring operations. nearer. therefore, to the producing levels, the relative quantity of mackinawite decreases and is compensated by pyrrhotite. On the riser pipes, which make up the last 200 m of production well and which are protected from corrosion by a synthetic rubber coating iron sulphide scale predominates (i.e., 92% pyrite for 6% greigite). The pressure in the wells (production or injection) can vary from 205 bars in the bottom of the wells (usually 160-180 bars) to 1 bar at the well head of the production well and around 10 bars at the well head of the injection wells. Mineralogical analyses show that all of the natural phases of iron sulphide coexist along all of the length of the wells. This shows that pressure does not play an important role in the precipitation of one phase rather than another or that it has no influence on the evolution of one phase towards another. On the other hand. it surely plays a role in the texture and density of scale idenser under high pressure). There is more calcite at the bottom of the well and the same is true for inorganic carbon (CO_3^{2-}) Within the range of temperatures encountered (45 to 85°C in the production well and 85 to 30°C in the injection well). the iron sulphide is stable and can coexist and precipitate. Temperature in the Dogger aquifer is not a determining factor in the precipitation of one phase rather than another No correlation was seen between the pH and the Eh of the fluid in a well and the nature and abundance of the scale formed on the walls of this same well Chemical calculation codes nevertheless show that the pH and the Eh vary very little in the well. except in the case of degassing Small variations in these two parameters within the same fluid or from one fluid to another have no effect on the stability of the iron sulphide formed under these conditions. In fact, local (within the scale or on the metal) or large variations in pH and Eh can occur and explain the formation of different phases of scale. There is a clear correlation between the sulphide content and the amount of scale on the walls (Fouillac *et al.*, 1989, 1990). The total iron and sulphide contents in the fluid control the amount of scale as well as the Fe/S molar ratio in the mineralogical structures of this scale. Indeed, a high total iron content in a fluid corresponds to a scale richer in pyrite and the same is true for hydrogen sulphide Although there are very few SRB in the circulating fluid (several cells per ml of fluid), they are present in the scale and are more abundant on the scale from the bottom of the well than from surface scale (428 cells/ml at -400 m and 8000 cells/ml at -600 m, from Honegger *et al.*, 1988). Furthermore, the $\delta^{34}S(S^{2-})$ of the scale sulphide is, in some wells, lower than that of dissolved sulphide in the fluid. This shows the bacterial origin of part of the sulphide which creates scale (Ignatiadis, 1994) Regarding the chemistry of the scale, iron and sulphur represent. respectively. 40 to 55% and 20 to 35% of the total weight of the scale for samples coming from the upper part of the casing. In the samples from the bottom of the well these percentages are lower and compensated for by the calcium and the silica This is in agreement with results from XRD.

3. DISCUSSION

The origin of mineral phases attached to a specific place on the casing wall can generally be attributed to

1) the precipitation of different mineral phases from dissolved iron (coming from the reservoir and corrosion) and anions (sulphides coming from the reservoir or from recent bacteriological activity, bicarbonates, chloride) contained in the fluid,
2) the migration of scale created and deposited at one place in the loop to another place, by erosion,
3) the transport by the fluid of particles from the reservoir which migrate and are deposited at different places in the loop,
4) the evolution of one phase towards another according to thermodynamic and kinetic laws, and influenced by the physico-chemistry of the fluid which may vary from one place to another (confinement. bacterial development, single or two phase medium and the resulting change in pH) and by variable operating conditions

We have seen that scale recuperated during the rehabilitation of some geothermal wells were made up of 70% of iron sulphides (with a majority of mackinawite). The operating conditions of the Dogger geothermal fluid, though, are such that the circulation rate is considered to be high and the maintaining of the fluid at a pressure higher than the bubble point prohibits the degassing of the fluid Knowing the physico-chemical characteristics of geothermal fluids, it is of interest to compare the observed scale with results of research concerning water with similar temperature, pH and composition and to try to determine the mechanism of formation of the various iron sulphides making up the scale.

The work of Meyer *et al.* (1958) on corrosion of soft steel in the H_2O-$NaCl$-CO_2-H_2S system arrived at the formation of mackinawite at the end of a 20 week test The authors attribute the nature of the corrosion product to chloride ions and to CO_2. The same corrosion test carried out in a H_2O-H_2S medium produces a very small amount of mackinawite Sardisco and Pitts (1965a) studied the kinetics of the steel corrosion reaction in the H_2S-CO_2-H_2O system and found that adding FeS to the corrosive system altered the nature of the iron sulphide film formed. These same authors (1965b) studied the corrosion of new and precorroded steel in the H_2S-CO_2-H_2O system and the composition and protective effect of the iron sulphide film formed. They sought to determine which of the bivalent sulphide species (H_2S, HS^-, S^{2-}) controlled the alteration of the iron sulphide film, knowing that the concentration of these bivalent sulphides were variable Two approaches were used· a) studying, at different pH. the composition and protective ability relative to the iron sulphide film formed during the corrosion of steel by the H_2S-CO_2-H_2O system. b) determining which. if any. of the bivalent sulphide species contributed to the decrease in protection of the iron sulphide film. The study showed that the nature of the corrosion products depends on the initial pH of the corrosive solution In the pH range between 6 6 and 8 4. mackinawite is the main component of the film. while for pH between 4.0 and 6 3 and between 8 8 and 11. mackinawite. pyrite, marcassite and troilite are present in the scale with still rather more mackinawite Weight loss measurements showed that mackinawite produces the least protective iron sulphide and that the protection was minimal in the pH range between 6.5 and 8.8 Knowing that in this pH range HS^- is the dominant dissolved sulphide species, it is logical to attribute to it the formation of non-protective iron sulphide scale. The change in the nature of the corrosion product had already been observed by Médicis (1970a, 1970b) Shoesmith *et al.*, (1980) studied the formation of ferrous monosulphide polymorphs during the corrosion of stainless steel by aqueous hydrogen sulphide at 21°C. They observed that troilite and cubic FeS formed between pH 3 and 5 whereas mackinawite was more abundant at higher pH values (from 6 to 7). Similar results had been obtained earlier at 50°C by Takeno et al. (1970). By examining the textures of their products, Shoesmith *et al.* (1980) concluded that mackinawite formed by surface reaction of dissolved Fe^{2+} and aqueous H_2S Murowchick and Barnes (1986) studied the formation of cubic FeS in deoxygenated and deionized water saturated with H_2S, and the pH was adjusted by adding HCl. H_2SO_4 or NaOH They report that cubic FeS and troilite formed by reactions between aqueous H_2S and Fe^{2+} (below 92°C, between pH 2 and 6), but mackinawite formed by reactions involving solid phases such as Fe metal or previously formed cubic FeS. Above 92°C, troilite and/or mackinawite were the only products Above pH 6, mackinawite was the only product. Tewari *et al.*, (1979) studied corrosion and scaling of carbon steel in an aqueous H_2S solution at 120°C and 16 bars They concluded that fluid velocity affects the nature of the iron sulphide film formed on carbon steel surfaces exposed to H_2S solutions Mackinawite is the predominant phase of the surface film formed at high fluid velocities but it transforms into pyrrhotite and pyrite at low velocities or in stagnant solution. Transformation of mackinawite to pyrrhotite and pyrite is accelerated in films under gaseous H_2S bubbles. The thin film of liquid between the bubble and the carbon steel-FeS interface acts as a relatively stagnant layer of Fe^{2+} ions. thereby maintaining a saturated condition with respect to Fe^{2+} ions which induces a rapid sequence of reactions leading to the formation of pyrrhotite and pyrite phases. Considering the geothermal fluids of the Dogger of the Paris Basin. Criaud *et al.*, (1989) studied their oxidation-reduction state and consequences for the prediction of corrosion and sulphide scaling Based on the pH-redox potential diagrams of iron (Pourbaix. 1964. Pound et al 1985). the authors observed that at 60 and 80°C, pyrite, Fe_3O_4 and $FeCO_3$ are stable, when the instantaneous potential (as measured) is considered Since pyrrhotite and other sulphides are definitely present, the authors admit that more reducing conditions may exist in the local environment. Alternatively to the Eh-pH diagram approach, the saturation indexes were calculated. Regardless of the choice of Eh as an input value in the models. the fluids were found to be close to saturation with respect to siderite, mackinawite, amorphous FeS, pyrrhotite and cubic FeS. This was in agreement with the iron-bearing minerals found during rehabilitation operations. Although saturation indexes for pyrite, marcasite, greigite and Fe_2S_3 depend on the redox potential, large over saturation was always obtained, decreasing when more reducing conditions are imposed in the model. The coexistence of pyrite/mackinawite/pyrrhotite implies that the iron sulphide can precipitate in an appreciably more reducing environment than might be expected from redox potentials used in the calculations (measured instantaneously, or estimated from redox couples). Moreover, the direct formation of pyrite and pyrrhotite is likely to occur while corrosion of the steel is proceeding. The mechanisms that account for iron sulphide scaling are complex and are not equilibrium processes. Recent studies (Ignatiadis *et al.,* 1994) allow us to calculate, as a function of temperature, the value and variations in the ionic activity product of the iron sulphide controlling the solubilities of iron and sulphides dissolved in the geothermal fluids and to identify the type of iron sulphide by comparing its ionic activity product (Q_S) to values of solubility products (K_S) given in the literature, taking into account observations on scaling. The values of pQ_S obtained using experimental precipitation data show over saturation with respect to iron sulphides at all temperatures. These pQ_S values are close to the pK_S values for amorphous iron sulphide. The pQ_S values obtained in real fluids. however, are close to those of the pK_S of mackinawite. This shows that, despite the presence of pyrite. pyrrhotite, greigite and marcasite in the scale on filters after filtration of the fluids, the iron sulphide that controls the solubilities of the dissolved sulphide and iron in the geothermal fluids is mackinawite. This is in agreement with the predominance of mackinawite in the scale deposited on the walls of the wells in question. Studies dealing with the phenomena of iron sulphide scaling on casing walls of wells exploiting the Dogger aquifer of the Paris Basin and research work carried out in the laboratory (Rickard, 1975; Tewari *et al.,* 1979: Shoesmith *et al.,* 1980; Wikjord *et al.,* 1976) show that Fe^{2+} and HS^- ions react together either in solution or on the surface of the corroded steel in order to form iron sulphide. In solution. the reaction leads mainly to the formation of amorphous iron sulphide (Ignatiadis and Peyrot, (1994) which then transforms into mackinawite. On the walls of the corroded steel, the reaction leads directly to the formation of mackinawite. For Berner (1967), in the presence of SRB, mackinawite can transform into pyrite when in contact with elemental sulphur. Amalhay *et al.,* (1994) showed that the predominant iron sulphide on stainless steel and titanium coupons was pyrite. This iron sulphide can only be exogeneous, therefore transported towards the coupons by the fluid either as pyrite or in a more primitive state and evolving thereafter into pyrite

Based on theoretical and experimental studies carried out in the laboratory and on site, it seems certain today that at the casing-geothermal fluid interface, the corrosion reaction of carbon steel leads mainly to the formation of mackinawite. The pyrite comes in part directly from the reservoir and from an evolution on the casing walls. The pyrrhotite and the greigite seem to be products of precipitation and/or evolution in the casings. Indeed, the pH of the geothermal fluids is almost neutral (6.1-6.7) and at the metal/liquid interface where the corrosion takes place, the cathodic reaction by the consumption of H^+ ions tends to increase the pH locally, thus favouring the mackinawite. Furthermore, at the metallic wall the mass balance favours ferrous ions produced by the corrosion which forms the sulphides richest in iron, such as mackinawite. The fact that we find pyrite in the scale samples from the bottom of the wells, on the non corrodable samples and on the filters means that a large part of the pyrite (and marcasite) comes from the reservoir fluid. Indeed, the arrival in the geothermal loop of small particles (several fractions of µm) of iron sulphide (mainly pyrite) coming directly from the reservoir leads us to think that these fine particles might play a roll of activator of germination and of growth. On the other hand, we now know that the dissolved iron content in the reservoir is much higher than that calculated by the equilibrium with pyrite (Criaud *et al.,*1989; Ignatiadis and Abou Akar. 1992; Ignatiadis *et al.,* 1992). One of the main modes of evolution possible is that of dissolution-precipitation. This evolution is favoured when the medium changes from an acid pH to an alkaline pH. Knowing that the pH of the Dogger fluids is stable and almost neutral, this mechanism is improbable at the macroscopic scale and can only occur locally, i.e., where H^+ ion activity is clearly modified. This can occur in anodic zones where there is pitting - acid media - or in confined zones which favour the localised production of hydrogen sulphide by SRB Since the medium is perfectly reducing and anaerobic (total absence of oxygen), the transformation of mackinawite into pyrite and greigite is only possible when a product of the oxidation of sulphides, elemental sulphur, is present as the latter is necessary for this transformation. Polysulphides are almost entirely absent in the fluid

All of the bibliographic remarks and considerations and their confrontation with experimental results lead us to propose a mechanism for the formation and regulation of scale on the walls of wells based on the control (of formation and regulation) by the diffusion of anions (sulphide, bicarbonate, chloride) through the scale. Indeed. the distribution of the scale in layers of different composition and structure is proof of a mechanism of deposition and regulation of the "anionic insoluble scale" type described by Crolet (1988). The two layers have components with different solubilities, the most insoluble phases (iron sulphides) being in contact with the fluid. The most soluble and acid scale is on the interior, in contact with the metal (FeOOH, $Fe(OH)_n$ $FeCl_2$ etc.) This explains why the scale not only does not protect the metal, but also is itself corrosive This configuration shows the progressive depletion (from the fluid to the metal surface] of concentrations of anions which precipitate the Fe^{2+} ions. Although it appears paradoxical, the first phases to precipitate are those which are located on the inside Indeed, in the diffusion layer there are rapid and opposite fluxes of cation (Fe^{2+}) and anion (HS^-, HCO_3^{2-}, etc) diffusion. These fluxes induce concentration gradients which can lead to the depletion of some anions since the iron flux is very large compared to the anion flux coming in the opposite direction The first minerals which precipitate are the least soluble. the iron sulphides. But the corrosion continuously feeds the iron flux. Once all of the iron sulphide that can precipitate has precipitated (since we have a gradient of sulphides such that beyond the diffusion layer of HS sulphides, there are no more iron sulphides) the Fe^{2+} precipitates with the following anion which should be $FeCO_3$ and after having depleted the carbonate, it precipitates the oxides, hydroxides, oxychlorides and, finally the $FeCl_2$. This explains why, in wells which exploit fluids with a high HS^- content, if any layer of hydroxides exists in the scale, it is very thin, while the Fe_xS_x layer is thick. Hence, the idea of an insoluble anionic scale model and that the main flux (the main gradient) is that of Fe^{2+} which can deplete the anions which come to meet it, and thereafter there is a stratification of the scale in the inverse order of solubility of the mineral species

4. CONCLUSION

In order to provide answers to the corrosion and scaling problems in the geothermal installations exploiting the Dogger aquifer in the Paris Basin, the scale which has been deposited during as much as ten years of exploitation has been examined. The results of chemical and mineralogical analyses of scale, in particular on well casing at different depths, but also on heat-exchangers, corrosion coupons and the wellhead filters have been studied. The scale **is** composed mainly of iron sulphides, calcite, siderite, and of iron hydroxide and hydroxychloride. It has been observed that the nature, distribution and abundance of these phases is a function of the nature of the metal substrate upon which they have formed, of certain physicochemical parameters of the fluid, of the origin of the scale (depth) and of the operating conditions. These results, together with those from the study of the conditions of formation of the various phases has made it possible to explain the origin, certain conditions of formation at the site and the relative abundance of the different phases Mackinawite. pyrrhotite, greigite, siderite, and iron hydroxides and hydroxychlorides are products of casing corrosion, whereas pyrite, silica, quartz and marcasite originate mostly from the reservoir itself in the form of micrometer-sized euhedral particles. The major scale layers has been identified and finally, a model of scaling control, suggesting that the formation of scale is controlled by the diffusion of anions (HS^-, HCO_3^-, Cl^-) is proposed

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REFERENCES

Abou Akar A. et Lafforgue M. (1994). Etude de la corrosion par coupons en acier au carbone places en zones monophasique et diphasique sur la centrale géothermique de Chelles (Seine et Marne). Rapport BRGM n° R 37832 GGP DR 94, 91 p.

Amalhay M., Gauthier B., Ignatiadis I. (1994a). The influence of some physico-chemical parameters and exploitation conditions on corrosion and scaling in geothermal wells in the Paris Basin. In *Proceedings of the International Symposium. Geothermics 94 in Europe, from Research to Development*, BRGM (ed.), Orleans, France, 8-9 February 1994, pp. 233-240.

Berner R. A. (1967). Thermodynamique stability of sedimentary iron sulfides. Am. J. Sci., Val. 265, p. 773-785.

Criaud A., Fouillac C. (1988). Sulfide scaling in low enthalpy geothermal environments: A survey. Geothermics, Special Issue, Vol. 18, n° 1/2.

Criaud A., Fouillac C., Marty B. (1989). Low enthalpy geothermal fluids from the Paris basin: 2. Oxidation-reduction state and consequences for the prediction of corrosion and sulfide scaling. Geothermics, Vol. **18,** n°5/6, p. 711-727.

Crolet J.L. (1988). Mecanismes de la corrosion uniforme sous dépôt de corrosion, Métaux Corrosion Industries, Vol. LXIII, n°757, pp. 279-302.

De Medicis R. (1970a). Une nouvelle forme de sulfure de fer. Revue de chimie minerale. vol. 7, p. 723-728.

De Medicis R. (1970b). Cubic FeS, a metastable iron sulphide. Science. vol. 170, p. 1191-1192.

Fouillac C., Criaud A., Honegger J.L., Czemichowski-Lauriol I. (1989). Sulfide deposition and well clogging in the Dogger aquifer of Paris Basin (France). European Geoth. Update, Florence, (Italie), Avril 1989, EEC Contract n° EN3G0033F.

Fouillac C., Fouillac A.M., Criaud A. (1990) Sulphur and oxygen isotopes of dissolved sulphur species in formation waters from the Dogger geothermal aquifer, Paris Basin, France. Applied Geochem. Vol. **5,** N° 4 p.415-427.

Honegger J.L., Guezennec J., Criaud A., Traineau H., Fera Ph. (1988). Corrosion en milieu géothermique. Approches métallographique et bacteriologique. Proceedings of the Congress on Bacterial Corrosion, 13-36 sept. 1988, Paris.

Ignatiadis I., Cheradame J.-M., Brach M., Castagne S., Guezennec J. (1990). Reduction by biocide treatment of hydrogen sulphide concentration in a geothermal brine. In "Microbially influenced corrosion and biodeterioration". Ed. N.J. Dowling, M.W. Mittelman, J.C. Danco. Proceedings or the International Congress on "Microbially Influenced Corrosion" Knoxville USA 7-12 october 1990, section 8, p. 33-36.

Ignatiadis I., Abou Akar A. (1992). Prelevement dechantillons de fluide geothermal en fond de puits de production au moyen du preleveur de fond PRINPIMO sur le site de Ris Orangis. Rapport BRGM n° R 36055 IRG SGN 92, 68 p.

Ignatiadis I., Abou Akar A., Lafforgue M., Bray Ph., (1992). Prelevement dechantillons de fluide geothermal par le tube dinjection dadditifs en fond de puits de production sur le site d'ORLY I. Rapport BRGM n° R 34513 IRG SGN 92, 76 p.

Ignatiadis I., Cheradame J.M., Lafforgue M., Castagne S. (1991). Evolution des teneurs en sulfures dissous dans les fluides geothermaux. Rapport BRGM n° R 33518 IRG SCN 91, 160 p.

Ignatiadis I., Detoc-Karimi S., Falguere P., Foucher J.C. (1992). The use of Cross-Flow microfiltration for the determination of solid suspended matter concentration and for the elimination of the sulphur produced by oxydation of dissolved sulfides in a geothermal brine. Proceedings of the Euromemhranes 92, October **5-8,** 1992 a Paris, France, in Récents progrès en Genie des procédés, Membranes Processes, P. AIMAR and P. APTEL Editors (Lavoisier Press), N°21, VOl.6, p. 141-146.

Ignatiadis I., Peyrot N. (1994). Estimation of the solubility product of the iron sulphide controlling the solubilities of iron and disolved sulphides in geothermal fluids from production wellheads in the Paris basin. To be submitted in Chemical Geology.

Ignatiadis I. (1994). Origins of the increased sulphide concentrations noted in geothermal fluids at production wellheads in the south and east of the Paris basin. In: *Proceedings of the International Symposium, Geothermics 94 in Europe, from Research to Development,* BRGM (ed), Orleans, France, 8-9 February 1994, pp. 241-248.

Mac Donald D.D., Roberts B, Hyne J.B. (1978). The corrosion of carbon steel by wet elemental sulphur. Corrosion Science, vol. 18, pp. 411-425.

Marty B , Criaud A , Fouillac C (1988) Low enthalpy geothermal fluids from the Paris sedimentary basin 1 Charactenstics and origin of gases Geothermics, Vol , 17, n° 4, pp 619-633

Meyer F H , Riggs O L , Mcglasson R L , Sudbury J D (1958) Corrosion products of mild steel in hydrogen sulphide environments Corrosion, Vol 14, n° 2, p 69-75

Murowchick J B , Barnes H L (1986) Formation of cubic FeS Am Mineralogist, Vol 71, p 1243-1246

Pourbaix M. (1964). Atlas of Electrochemical Equilibria Pergamon Press, London.

Pound B.G., Abdurrahman M.H., Glucina P., Wright G.A., Sharp R.M. (1985). The corrosion of carbon steel and stainless steel in simulated geothermal media. Aust. J. Chem., Vol. 38, p.1133-1140.

Rickard D.T. (1975). Kinetics and mechanism of pyrite formation at low temperatures. Amer J. of Science, Vol. 275, p.636-652.

Rojas J. et al. (1989). Caracterisation et modelisation du reservoir geothermique du Dogger, Bassin Parisien, France. BRGM-CCE. Rapport R 30169 JRG SGN 89,240 p

Sardisco J.B. and Pitts R. E. (1965a). Corrosion of iron in an H_2S-CO_2-H_2O system: mecanism of sulfide film formation and kinetics of the corrosion Reaction. Corrosion, Vol. 21, N°8, p. 245-253.

Sardisco J.B., Pitts R.E. (1965b). Corrosion of iron in an H_2S-CO_2-H_2O system - composition and protectiveness of the sulphide film as a function of pH. Corrosion, NACE, Vol. 21, n° 11, p. 350-354.

Shoesmith D.W., Taylor P., Bailey M.G., Owen D.G. (1980). The formation of ferrous monosulphide polymorphs during the corrosion of iron by aqueous hydrogen sulphide at 21°C. Electroch. Soc.J., Vol. 127, p. 1007.

Takeno, Sesuo, Zoka, Hisanori, Niihara, Toshihiro (1970). Metastable cubic iron sulfide-With special reference to mackinawite. American Mineralogist, 55, p. 1639-1649.

Tewari P.H., Bailey M.G., Campbell A.B. (1979). The erosion-corrosion of carbon steel in aqueous H_2S solutions up to 120°C and 1.6MPa pressure. Corrosion Science, 19, p. 573-585.

Wikjord A.G., Rummery T.E., Doern F.E. (1976). Crystallisation of pyrite from deoxygenated aqueous sulfide solutions at elevated temperature and pressure. Canadian Mineralogist, Vol. 14, p. 571-573.