

# Scale Prevention with Sodium Tripolyphosphate as Inhibitor

Mioara Sebeșan<sup>\*</sup>, Oana Stănășel<sup>\*</sup>, Aurel Iovi<sup>\*\*</sup>

<sup>\*</sup> University of Oradea, Department of Chemistry, Oradea, Street Universitatii, No.5, Romania

<sup>\*\*</sup> POLITEHNICA University of Timișoara, Department of Technology, Timișoara, Romania

Mioara Sebeșan, e-mail: msebesan@uoradea.ro

Oana Stănășel, e-mail: stanasel@uoradea.ro

**Abstract:** The chemical composition of geothermal waters depend on the mineralogical structure of the geological formations of the reservoir. Due to the pressure drop at the wellhead and due to temperature changes during utilization there could appear scaling problems.

Deposition samples from three geothermal wells were collected and analysed. They are formed by calcium carbonate as main. They also contain traces of  $MgCO_3$ ,  $Al_2O_3$ ,  $Fe_2O_3$ ,  $CaSO_4$ . This paper present the possibility of scale control by using sodium tripolyphosphate as inhibitor.

**Keywords:** well, treatment with inhibitors, tripolyphosphate

## 1. Introduction

The geology of the reservoirs and the geothermal waters characteristics are correlated. There were identified three types of waters in the western geothermal area of the country: sodium-potassium-bicarbonated waters at Salonta with a tendency to become sodium-potassium-chloride waters in Ciumeghiu, calcium-sulphate type in Oradea and sodium-bicarbonated in Jimbolia zone. The mineralisation of these waters varies from a zone to the other.

There were taken for study the following geothermal wells from the Western Plain of Romania: wells 4632 and 4636 from Lovrin and well 4156 from Borș. There were recorded scale formations during exploitation due to deposition from waters and due to the corrosion of the pipes.

In order to prevent scaling there were made inhibition tests with sodium-tripolyphosphate.

## 2. Experimental

Geothermal waters from the studied geothermal wells were analysed. The chemical composition is presented in tables 1 - 3.

The methods of analysis are presented as follows:

*Determination of hydrogen sulphide [7].*

$H_2S$  determination was made by titration with  $Hg$ -acetate in presence of dithizone. In this purpose 45 ml of sample were combined with 5 ml of 5N NaOH solution in a volumetric flask. This content was added to 5 ml acetone into an Erlenmeyer flask.

The solution was then titrated with  $(H_3CCOO)_2Hg$  in presence of small grain of solid dithizone. During titration a black precipitate of  $HgS$  forms. The endpoint is recorded when the colour changes from the yellow colour of dithizone in alkaline solution to the red colour of the  $Hg$ -dithizonate. If the concentration of hydrogen sulphide is high the sample becomes yellowish brown and even black during titration.

This is caused by the  $HgS$  precipitate and makes the

endpoint uncertain. In this case is better to reduce the volume of the sample.

*Determination of chloride [6].*

The analysis was made by titration with silver-nitrate solution, 0.01M, using potassium chromate as indicator.

The colour changes from yellow to brown, but the colour change is very difficulty to identify. Before titration the pH must be checked to be above 8.2. If it is not, 1N NaOH solution is added drop by drop.

*Determination of sulphate [6].*

The analysis was made by precipitation with barium perchlorate in presence of thorin. The method is based on the titration of the exces of barium perchlorate solution until the first colour change from yellow to pink.

*Determination of carbon dioxide [7].*

The analysis is made by titration. The water sample is treated with a mineral acid.

The free carbon dioxide, the released  $CO_2$  from carbonates and bicarbonates are drawn into air and absorbed in a 0.02 N  $Ba(OH)_2$  solution. After the formed precipitated is filtered, the exces of  $Ba(OH)_2$  is titrated with 0.02N HCl by using phenolphthaleina as indicator.

Determination of phenols was made by using spectrophotometric method. The absorptions were read at 435nm.

*Determination of silica [6].*

The spectrophotometric method is based on the reaction of silica with molybdate ions at pH of 1.2-1.5. A yellow silico-molibdate complex is formed. If the concentration of silica in thermal water is higher than 100 ppm, the silica can polymerize and the polymerized silica will not react with molybdate. Treatment with alkali converts it all to the monomeric state. The adopted procedure covers the concentration range of 20-500 ppm. Higher concentrations can be determined by taking smaller aliquots. A disadvantage of this method is the instability of colour of the solution. For this reason the samples and the standards must be prepared at the same time and the absorption must be read 10-60 minutes after developing the colour. High concentration of hydrogen sulphide may

reduce the silicomolybdate complex to molybdenum blue. This can be prevented by oxidizing the sulphide with iodine.

#### Determination of sodium, magnesium and calcium [6].

The analysis of these components were made by atomic absorption spectroscopy.

For the determination of these dissolved constituents the samples must be filtered and acidified with 4 ml of suprapure  $\text{HNO}_3$  per liter of sample. A Cs-La solution is added to samples, blank and standard solutions. Ionization should be controlled by the addition of Cs-La solution and oxysalt interference on calcium is reduced.

The solutions are directly aspirated into an oxidizing air-acetylene flame. Absorptions are read at 589.6 nm for sodium, at 766.5 nm for potassium, at 285.2 nm for magnesium and at 422.7 nm for calcium.

The solid depositions formed on the equipments during utilization were analysed and the results are shown in table 4. After chemical treatment with 5 mg/l tripolyphosphate, the deposition was insignificantly.

TABLE 1. Characteristics of geothermal waters from Lovrin, well 4632 in mg/l.

Chemical characteristics	Deep water	Wellhead water	After degasing
pH	7,5	8,1	8
Na	939	941	855,6
Ca	9,5	14,95	19,5
Mg	4,2	5,1	5,9
Cl	636	637	505
$\text{SO}_4$	7,01	14,2	26,9
$\text{HCO}_3$	1429	1420	1440
$\text{H}_2\text{S}$	1,94	1,04	1,54
$\text{Al}_2\text{O}_3$	13	1,8	4,8
$\text{Fe}_2\text{O}_3$	0	5	0
$\text{SiO}_2$	61,9	58,5	41,2
TDS	2985	2963	2670
$\text{CO}_2$ (aggressive)	0	0	0
$\text{CO}_2$ (free)	18,2	0	0

TABLE 2. Characteristics of geothermal waters from Lovrin, well 4636 in mg/l.

Chemical characteristics	Deep water	Wellhead water	After degasing
pH	7,9	8	8
Na	850,9	946,7	98
Ca	28,4	26,6	25,6
Mg	2,9	5,7	9,5
Cl	1055	1069	600,9
$\text{SO}_4$	15,15	8,2	16,5
$\text{HCO}_3$	1169	1160	1248
$\text{H}_2\text{S}$	2,02	1,84	1,92
$\text{Al}_2\text{O}_3$	8,71	8,9	16,3
$\text{Fe}_2\text{O}_3$	1,54	0	0
$\text{SiO}_2$	30,2	34	50,2
TDS	4116	3120	2755
$\text{CO}_2$ (aggressive)	0,15	0	0

TABLE 3. Characteristics of geothermal waters from Borș 4156, in mg/l.

Chemical characteristics	Deep water	Wellhead water	After degasing
pH	7,7	8,3	7,2
Na	1256,8	1123,6	1786,8
Ca	17,9	15,8	12,5
Mg	11,8	6,89	22,4
Cl	832,7	743,8	437,9
$\text{SO}_4$	30,9	19,8	18,6
$\text{HCO}_3$	2309,6	2276,6	1651,2
$\text{Al}_2\text{O}_3$	3	43	18,7
$\text{Fe}_2\text{O}_3$	2,5	0	1,5
$\text{SiO}_2$	98,7	62,5	110,8
TDS	12489,5	12401,2	12334,8
$\text{CO}_2$ (aggressive)	33,2	0	0
$\text{CO}_2$ (free)	2,25	0	0
Chemical characteristics	Deep water	Wellhead water	After degasing

TABLE 4. Chemical composition of scale deposits

Component	Well 4632	Well 4636	Well 4156
CaO	51,95	52,18	53
MgO	0,63	1,98	0,61
$\text{SO}_4$	0,43	0,38	0,89
$\text{SiO}_2$	0,08	0,018	0,28
$\text{Fe}_2\text{O}_3+\text{Al}_2\text{O}_3$	4,3	1,81	1,78
$\text{CaCO}_3$	92,76	93,1	94,6
$\text{MgCO}_3$	1,32	4,16	1,28
$\text{CaSO}_4$	0,47	0,41	0,97

### 3. Results and discussions

In order of getting a proper method to control scale, the geothermal waters and the solid depositions were analysed.

Depositions were found both in the pipe inside the well, having a thickness of 30-50 mm at the wellhead and in the connection equipments from the surface. The deposition thickness is bigger before the degasing system than after it. At geothermal wells from Lovrin the thickness of the deposition was in the range of 30-40 mm inside the pipe before the degasing and between 1,5 and 32 mm after it. The main component of the deposition samples is calcium carbonate. Its concentration is about 92,76-93,1% at Lovrin and 94,6% at Bors. Because the decomposition temperature of calcium bicarbonate is high,  $\text{CaCO}_3$  in the solid samples is mainly crystallized as aragonite. The other components of the solid depositions, in weight percent are:  $\text{SiO}_2$  in a range of 0,08-0,28%,  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  in 1,81-4,3%,  $\text{MgCO}_3$  from 1,32 to 4,16% and  $\text{CaSO}_4$  from 0,41 to 0,97%. The addition of tripolyphosphate in a dosage of 5 mg/l inside the well is followed by an important decrease of the rate of growth of scale. This is shown by the data from last column of table 4.

#### 4. Conclusions

The geothermal waters from the wells from Lovrin have a lower mineralisation than the waters from Borș. The chemical composition of these waters allow to establish the type of water: bicarbonated-sodium-chloride.

The chemical analysis of the depositions formed during utilization indicated a high concentration of calcium, the scales being calcium carbonate as main.

The scale deposits in the pipeline are more voluminous inside the well towards the surface and at the degasing entry. This could be due to flow variation, pressure and temperatures changes during exploitation of the well.

In order to avoid a plug in the pipeline system at well 4632 from Lovrin, were made the installations for testing with inhibitors. It was used tripolyphosphate as inhibitor. By modifying the concentration it was found out that a low concentration of 5 mg/l is efficient to prevent scale formation.

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