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Formation and protection against incrustation on the geothermal pipe by utilizing of geothermal water in the area of Ďurkov (Eastern Slovakia)

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Presented contribution describes reasons for rising of rusting and incrustation and possibilities of its removing at the technological equipment during use hot geothermal water from the locality Ďurkov. The village Ďurkov is situated in the eastern part of the Košice Basin (15 km from the city of Kosice) that belongs to one of the most significant and most perspective areas with geothermal waters in Slovakia. Geothermal waters in Ďurkov are bound to Triassic dolomites located in the basement of Neogene sediments. The biggest attention is paid to the choice of the most modern methods for treatment with hot geothermal water, either by chemical or by physical processes and further attention is paid to the geothermal energy system and its parts that are subjected to the rusting and incrustation, the important results of physical-chemical measurements, the values of the elements contained in hot geothermal water. The objects of the scientific research works are also protection of geothermal equipment (geothermal pipes) against incrustation, methods – possibilities of its removing, high mineralization of geothermal water and its elimination. Modern technologies and research acknowledge that problems associated with using of geothermal energy are no more unsolvable. Trend and practice confirm that from the mentioned measures for inhibition of the incrust and rust formation on metallic parts, the equipment CALC-TECH CT-19252 N electronic will play an important role in this industry.

Key words: *geothermal well, geothermal water, renewable energy source, geothermal potential, geothermal equipment, well completion, inhibitor, incrustation, corrosion, methods of rust removing.*

Introduction

Geothermal energy is one of the most important energy sources in the world, but locally can be also very important and able to replace traditional non-renewable energy sources – fossil fuels that are rapidly consumed, but also have a negative impact on the environment.

Geologists and workers in the power industry have paid attention to the problems of the earth´s heat and its potential using as energy sources for many years. Almost 35 – year - old petroleum research in eastern Slovakia has played an important role in this area. In this connection drill holes were realized that have penetrated to the deep of several kilometres. The mentioned drilling works enable to get to know the rock composition of the investigated area (Hudeček et al., 2013, Wachowicz, 2015) and other data that are connected with the tasks of the eventual possibility of geothermal energy obtaining, remain applicable ideas only on theoretical even hypothetical level (Wittenberger, Pinka, 2004, Cehlár et al., 2014). The southern part of Košice valley is famous for the existence of geothermal sources of considerable energy capacities, which are the largest not only in Slovakia but in the whole eastern and central Europe. Nowadays, the intentions of using of this available source are reversed on the locality Ďurkov near Košice, figure 1, where three deep geothermal wells were drilled off in 1998 and 1999 - one vertical GTD-1 and two directed GTD-2 and GTD-3 – (GTD -1,2,3).

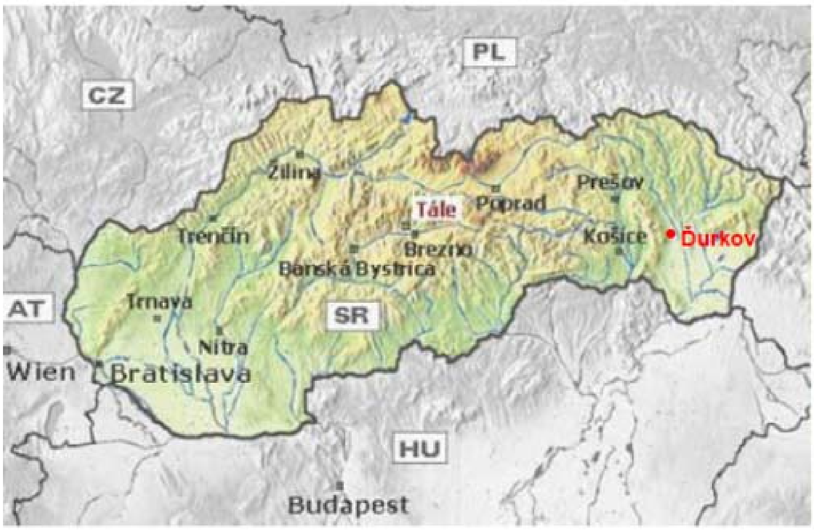

Fig. 1. Locality of geothermal wells GTD 1,2,3 - near the village Ďurkov.

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Inhibitors used in geothermal waters

On the basis of results from pumping tests and physical-chemical analyses it has been discovered that geothermal water is strongly mineralized and depending on the way of its manipulation and exploitation it is apt to formation of incrusts and it also have a considerable corrosive ability (depending on state values p and t). To prevent from the undesired formation of corrosion and incrustation following inhibitors of geothermal water have been tested: SP2556 (Baker Petrolite), Inipol AD 15 (CECA France), Stabil 2000, Ankodis 6. The company Slovgeoterm a.s. Bratislava has provided in Table 1 a total mineralization of geothermal waters from wells GTD -1,2,3 in average values, while several measurements were taken and measured values differed slightly (Bandurová et al., 1999, Rijkers, et al., 2014).

Origin and protection of geothermal equipment against corrosion and incrust creation

One of the big problems in the treatment of the geothermal water from geothermal wells GTD 1,2,3 is the elimination of considerably high mineralization, which is approximately 31 $g.l^{-1}$ while in some countries using geothermal energy this value would be almost insignificant. In Latvia near the town Klaipedsa they use geothermal water with mineralization 160 to 220 $g.l^{-1}$ which has a high content of calcium sulphate (if geothermal water is not treated with inhibitor, gypsum is separated from it in a distribution system), in Danish Thisted and in some locations in Germany mineralization values reach 240 $g.l^{-1}$ (Geroč, 1999, Dogan, 2014).

Application of the inhibitor into the geothermal water does not decrease mineralization but slightly increases (inhibitor substance is added), its main function is to participate in the formation of crystalline cores and microcrystals and then deforms and disrupt them (Buyuksagis, 2013, Verma, 2013). There is a constant formation and immediate disintegration of a crystal. Effect mechanism of incrustation inhibitors lies in the fact that they accelerate the formation of crystalline nucleus centres where a large amount of little crystal forms and that they unfavourably affect growth of crystals in a crystal lattice. Crystal growth is slowed down, a crystal lattice is deformed, forming crystals has an irregular shape and instead of compact and solid layer an amorphous and incompact layer is formed, resp. it is formed in a a smaller amount or not formed at all.

Molecules of inhibitor adsorb to a surface of the crystal, while part of the molecule remains desorbed and a layer preventing from clustering and uniting of crystals is formed (Galamboš, et al., 2012, Galamboš, et al., 2015, Kačur et al., 2014).

In order to keep calcium compounds in dissolved state it is necessary to keep CO_2 partial pressure at the wellhead above the value 2,9 MPa which means that the pH of geothermal water at the wellhead may not rise above 5,53 (in a closed pressurized system and untreated geothermal water) (Gryc, 2014, Ning, et al.,2012). During cooling of geothermal water in a heat exchange system under sufficient pressure water gradually becomes unsaturated regarding the calcium-carbonate system partly due to increase in $CaCO_3$ solubility with decrease in temperature and partly due to increase in CO_2 solubility at lower temperatures. The consequence of this is a substantial combined corrosion partly due to high content of dissolved gases, especially CO_2, as well as due to high concentration of chlorides, sulphates, hydrocarbons and ammonium ions at increased temperature and pressure. Due to the high amount of chlorides in addition to general corrosion also substantial pitting corrosion will appear (Beňovský et al., 2000). In case of not keeping necessary pressure in the system, formation of compact $CaCO_3$ deposits on walls of the piping and heat exchanger areas will occur. Its speed depends on level of degassing. Increased pH to 5,6 means a tendency to incrustation at temperatures ranging from 125°C to 97°C (which corresponds to CO_2 concentration of 7880 mg.l-1 at temperature of 125°C to 6300 mg.l-1 at 97°C), with pH 5,7 there is a danger of incrustation at temperatures ranging from 134°C to 70°C and above pH 5,7 in a whole range of temperatures considered for the heat exchanger system. (Stanković, N. J., et al., 2011).

Results of model tests and calculations have proved that for partially degassed geothermal water, for example, if it runs through a pressure degassing valve on the separator, water inclines to incrustation and achieves values above 110 mg.l-1.

Table 1. Mineralization geothermal water from wells GTD-1,2,3 (Beňovský et al., 2000).

Nr of samples	Well	M (mg.l^{-1})	pH	Fe	As	Pb	Li	Na	K	NH_4	Ca	Mg	Sr	Mn	F	Cl	I	SO_4	NO_2	HCO_3
16 198	GTD-1	29 745,24	7,150	4,500	36,70		37,240	9816,30	448,25	53,77	327,60	124,2	12,843	0,103	1,990	15 189,30	3,74	565,20	0,001	2 038,05
16 498	GTD-1	30 646,40	7,410	3,600	20,40		35,230	9876,70	448,00	60,15	527,20	160,4	15,500	0,242	2,610	15 688,30	4,91	577,55	0,001	2 135,70
16 798	GTD-1	29 948,54	6,970	1,322	20,65		36,275	10250,00	451,50	57,09	96,50	100,2	7,193	0,150	1,680	15 686,30	3,10	597,09	0,001	1 543,80
Average		**30 113,4**	**7,177**	**3,141**	**25,92**	**0,000**	**36,2**	**9981,00**	**449,25**	**57,01**	**317,1**	**128,3**	**11,845**	**0,165**	**2,093**	**15 521,3**	**3,92**	**579,9**	**0,001**	**1 905,9**
42 298	GTD-2	20 408,07	7,210	5,748	19,50	0,001	25,600	7005,00	359,50	30,64	265,50	55,30	13,800	0,154	2,210	10 580,19	2,34	464,80	0,001	1 510,25
40 898	GTD-2	25 663,31	6,870	4,141	27,71	0,025	29,500	8905,00	400,50	33,37	269,25	55,05	13,140	0,216	1,740	13 725,67	2,18	551,60	0,001	1 583,45
41 298	GTD-2	25 804,46	6,760	6,128	31,98	0,008	30,100	8990,00	399,50	35,94	191,35	51,70	10,370	0,211	1,950	13 903,50	3,13	550,40	0,001	1 537,70
41 198	GTD-2	25 209,96	6,890	6,011		0,028	30,000	8970,00	393,00	32,96	214,95	55,65	10,825	0,201	1,840	13 571,00	2,28	556,75	0,001	1 261,60
42 598	GTD-2	24 939,28	7,530	4,762	31,05	0,011	32,400	8780,00	446,50	37,64	202,85	54,90	9,290	0,177	1,940	13 364,45	2,36	532,90	0,001	1 385,15
Average		**25 404,25**	**7,013**	**5,261**	**30,25**	**0,018**	**30,50**	**8911,25**	**409,88**	**34,98**	**219,60**	**54,33**	**10,906**	**0,201**	**1,868**	**13 641**	**2,49**	**547,9**	**0,001**	**1 442,0**
42 698	GTD-2	29 039,94	7,430	2,304	33,28	0,008	38,350	10440,00	487,00	33,09	101,30	46,90	6,315	0,122	2,160	15 870,29	2,76	618,05	0,001	1 305,85
15 399	GTD-2	31 242,28	7,230	0,249	21,05	0,001	37,180	11096,00	533,80	52,41	178,40	41,40	13,487	0,027	2,010	16 856,90	13,44	652,65	0,062	1 671,95
15 599	GTD-2	31 185,07	7,300	0,120	25,18	0,003	37,600	11148,00	518,20	51,29	122,20	39,50	10,397	0,030	2,010	16 971,75	14,02	636,60	0,085	1 543,80
15 799	GTD-2	31 438,72	7,170	0,128	26,80	0,002	37,800	11180,00	522,20	53,38	163,30	42,55	13,227	0,079	2,230	17 010,75	18,46	660,65	0,050	1 635,65
44 400	GTD-2	30 351,45	6,910	3,288	35,35	0,007	35,418	10475,50	387,30	49,44	402,00	34,40	19,520	0,092	1,980	15 794,60	2,30	638,05	0,050	2 417,90
48 900	GTD-2	30 221,17	7,080	2,049		0,006	38,800	10585,00	449,00	47,98	335,50	34,10	17,710	0,065	2,790	15 682,70	3,52	659,20	0,011	2 257,70
49 300	GTD-2	30 336,73	7,120	1,881		0,005	36,670	10637,70	410,80	56,75	313,50	33,53	17,120	0,050	3,510	16 123,62	2,67	604,30	0,001	2 025,65
Average		**30545,05**	**7,177**	**1,431**	**28,33**	**0,005**	**37,40**	**10794,60**	**472,61**	**49,19**	**230,89**	**38,91**	**13,968**	**0,066**	**2,384**	**16330,09**	**8,17**	**638,50**	**0,037**	**1836,93**
7 299	GTD-3	32 043,42	7,120	11,11	36,50	0,155	36,400	11150,00	744,50	39,95	200,13	54,88	7,295	0,114	1,665	17 147,00	3,25	767,85	0,260	1 784,85
7 399	GTD-3	32 907,04	7,190	7,160	35,00	0,178	37,250	11600,00	694,00	40,78	194,12	54,27	6,265	0,094	1,653	17 764,00	2,98	729,00	0,001	1 682,10
7 499	GTD-3	32 562,23	6,650	2,130	35,40	0,229	39,820	11470,00	684,00	43,10	174,40	45,10	11,190	0,070	2,023	17 778,30	3,00	694,20	0,001	1 501,10
7 699	GTD-3	33 125,98	6,720	0,740	32,80	0,148	39,820	11780,00	686,00	42,78	128,20	44,20	8,930	0,058	2,035	18 066,90	3,01	693,40	0,028	1 525,50
Average		**32 659,67**	**6,920**	**1,435**	**34,93**	**0,178**	**38,32**	**11500,00**	**702,13**	**41,65**	**174,21**	**49,61**	**8,420**	**0,084**	**1,844**	**17 689,05**	**3,06**	**721,11**	**0,007**	**1 623,39**
5 101	GTD-3	31 652,72	6,760	1,385	19,23	0,002	35,440	11120,00	402,30	71,06	345,35	41,90	18,875	0,060	2,315	16 636,50	2,67	588,25	0,006	2 300,45
6 101	GTD-3	31 323,78	7,060	1,015	22,12		37,760	10931,50	417,20	56,39	348,70	47,42	18,770	0,059	2,100	16 594,30	2,73	610,25	0,044	2 160,10
Average		**31 488,25**	**6,910**	**1,200**	**20,68**	**0,002**	**36,60**	**11025,75**	**409,75**	**63,72**	**347,03**	**44,66**	**18,823**	**0,060**	**2,208**	**16 615,40**	**2,70**	**599,25**	**0,025**	**2 230,28**

It arises that in this way of using the geothermal water will keep the ability of incrustation also in a cooling process, quite substantially. At free atmospheric degassing with the decrease of CO_2 below 0,2 MPa geothermal water achieves supersaturation with free ions of calcium of 50 to 193 $mg.l^{-1}$ v within a whole range of temperatures that in a heat exchange system come into consideration. During a long-term test the geothermal water has been treated with inhibitor and etalons were not from common ductile steel, but from a casing steel grade J 55, therefore measured results are substantially different. When applying the inhibitor Stabil 2000, incrustation has occurred only before the heat exchanger and only as a discontinuous thin layer with an average thickness of 0,25 mm. Since incrustation has not been continuous secondary corrosion which is more dangerous has occurred.The inhibitor Stabil 2000 has proved to be unsuitable for treatment of geothermal waters of the Košice Basin, since it was sufficiently efficient only above doses of 90 $mg.l^{-1}$.

The inhibitor Inopol AD 15 proved to be universal because it totally suppressed incrustation at a dose of 90 $mg.l^{-1}$ and partially reduced also corrosion (Hrehová et al., 2013). For smooth use of mineralized geothermal water an inhibitor sodium hexametaphosphate with a commercial name Ankodis 6 will be sprayed into the well. It is a mixture product of non-ionic surfactants consisting of ethylene oxide and propylene oxide copolymer with a molecule weight of approximately 600 and ethoxylated octadecylamine which is a well proven inhibitor for this kind of geothermal waters (Ruiz-Agudo, C., 2014).

Chemical composition of sodium hexametaphosphate is evident from its name $Na_6P_6O_{18}$, which is an anodic inhibitor with excellent effect against incrustation and it can be classified as a so-called threshold inhibitor. It is sufficiently efficient at applied dose of 1 $mg.l^{-1}$. To intensify the effect of the inhibitor against corrosion we have to add zinc chloride and copolymer of acrylic acid (Sokrat 44), or acrylic and maleic acid (Sokrat 70), which substantially reduces corrosivity to 0,1 $mm.year^{-1}$. Adding Zn in small doses results in the formation of a thin layer of zinc on casing steel and thus it is protected also secondarily (Gonet et al., 1999).

Alternatively, during the well test also American inhibitor SP-2556 from the company Baker Potroline has been applied. The results were very good and price relation regarding the applied amount was excellent. It disintegrates after 20 days, so it does not affect quality composition of underground water in the reservoir in any way and it complies with the standards and requirements of the European Union. To eliminate corrosion and formation of incrusts inhibitor, which is transported to a depth of 300 m with a dosing pump located behind 4 m^3 tanks from which inhibitor is dosed, has to be applied into geothermal water. Total dosed amount in the production of the 2500 TJ per year represents 16-17 tons per year (Wittenberger, 2013).

The geothermal centre in Olšovany will have a storage of chemicals (they will be delivered and stored in barrels), where solutions will be prepared and delivered to individual centres in a small cistern. The tanks on the well will be refilled and from them solutions are injected into production wells with high-pressure pumps below evasion point.

The control module

CT 19252 N			
		1 output	2 outputs
Performance	W	240	480
Tube diameter	DN	<250	<350
Protection		IP 65	
Dimensions (W x H x D)	mm	3 height = 600 x 363 x 450	
Weight	Kg	35.0	

Fig. 2. Equipment CALC-TECH CT 19252 N electronic installed in the output pipeline with the control module.

These chemicals are not hazardous and time of their disintegration is max. 48 hours (Beňovský et al., 2000). On the outlet pipe from each production well the electronic-physical equipment CALC-TECH CT-19252 N electronics will be installed, which will serve for treatment of geothermal water, figure 2. It is equipment which prevents calcium crystals from forming clusters of acicular shapes with high cohesiveness.

Microscopic calcium particles remain in the water in their original size (10 µm) and acicular structures do not occur anymore. Therefore, they may not cluster and adhere to a surface of pipes and heat exchangers. Installation itself lies in winding six coils on the pipe right after its exit from the well. For this installation we need 2 m section of a straight pipe. Coils are connected to two generators. The first one is for production of impulses and the second one for varying impulse frequencies according to the flow rate of the geothermal water. By adjusting elements on a front side of the equipment CALC-TECH CT-19252 N electronic it is possible to adjust the equipment according to actual conditions (Keçebaş, 2014, Liang-he, 2013)

The frequency in function of the water flow measured by a flowmeter is controlled by Calc-Tech CT-19252 N. A Calc-Tech - the coils are situated on 5 different places and it helps in treating the complete factory against lime scale deposits. A Calc-Tech system is adjusted to the water speed through the pipes and installed just before circulating pumps. Geothermal energy is the perspective renewable energy source in the world. Areas of geothermal waters using for electricity production or heating are very actual mainly by a permanent rising of the energy prices, nowadays.

Conclusions

A lot of problems occur by using of geothermal energy. One of them is formation of incrusts and rust on metallic equipment. Modern technologies and research acknowledge that problems associated with using of geothermal energy are no more unsolvable. The problems may be solved by using and utilizing of the basic physical-chemical knowledge supported by progressive practical research (Sidorová, Pinka, 2007, Woyessa, 2012). All of the mentioned measures being used against the incrustation and rusting have advantages and also disadvantages, which ultimately is not a step forward in the prevention of the negative impact of geothermal water on the pipeline (Bujok et al., 2013).

Resume

With regard to the world trends Slovakia has been ranked among the states that try to use domestic geothermal sources also in spite of above mentioned high mineralization and some technical and economical problems, in the last time. Thanks to geological research works Slovakia belongs to the regions with above-average high geothermal potential. Analysis and tests have showed that from four inhibitors (SP2556, Inipol AD15, Stabil 2000 and Ankodis 6), that were used for pressing down of high mineralization, only inhibitors SP2556 and Inipol AD15 successfully passed the test. Trend and practice confirm that from the mentioned measures for inhibition of the incrust and rust formation on metallic parts, the equipment CALC-TECH CT-19252 N electronic will play an important role in this industry (Wittenberger, 2013).

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