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NEW POSSIBILITIES FOR THERMAL WATER TREATMENT

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In the well tube precipitation and scaling occur if the physical-chemical equilibria of the components dissolved in thermal water are disturbed partly due to cooling, but largely to the drop of pressure and subsequent gas evolution. All the known methods for the prevention of scaling have some disadvantages. This paper describes a novel technology which is economical and environmentally sound. Supersaturated $Ca(OH)_2$ suspension is pressed below the bubble point of the well tube and induces $CaCO_3$ precipitation. A unique feature of the process is that it takes place in the presence of excess acid since below the bubble point all CO_2 is dissolved in water. The pilot scale experiments resulted in products of industrial use.

Keywords: geothermal fluid, bubbling point, prevention of scaling

Introduction

In his recent paper [1] Sándor Papp wrote that 45% of incoming solar energy ($2{,}48.10^{24}$ J/a) is absorbed by oceans, continental and ice surfaces. Evaporation and convection returns $1{,}28.10^{24}$ J/a and $3{,}2.10^{23}$ J/a energy into the atmosphere. It is interesting to compare these values with the data given in a paper by Fanelli and Taffi [2] who evaluated the potential utilization of geothermal energy. They stated that about 10^{21} J/a energy was released through the surface of the Earth by heat conduction. Currently, however, the industrial utilization of geothermal energy is economical only in certain areas, from either liquid reservoirs with temperature in excess of 260°C (e.g. Wairakei, New-Zealand) or from geothermal reservoirs of dry or supersaturated vapor (Lardello and Mt.Amiata, Italy). Hungary does not have such a potential, but it has the second largest resources of low-enthalpy thermal water and a geothermal gradient of 1°C/15-18 m well above the global average. In about half of its area it is estimated to have thermal water resources of 70-98°C in the depth 1500-2500 m. However, as against the data for 1976 given by Balogh and Bökfi [3] indicating development, by the turn of the millennia the utilization of geothermal energy in both industry and agriculture declined considerably. The heating of homes with thermal water has raised a number of technical-financial problems, so now only secondary utilization seems to be economical. It follows that instead of primary utilization for energy production the emphasis is to be put on balneological and medical applications. On the basis of their experiments in Zalakaros, the authors propose a novel direction of potential development.

Characterization of thermal waters

The definition of mineral and medicinal waters was modified several times in the previous century. The Hungarian standard pending from 1995 defines natural mineral water as water from any well or closed spring which originates from subsurface aquifiers. The mineral water is pure by origin, it is microbiologically clean, has nearly constant chemical composition and temperature, has dissolved solid mineral content of at least 1000 mg/L, or, alternatively, if its mineral content is between 500 and 1000 mg/L, the concentration of sodium is less than 200 mg/L, and at least one of the following constituents of nutritional-physiological importance exceed the following limits: calcium 60 mg/L, magnesium 20 mg/L, fluoride 0,8 mg/L, iodide 0,05 mg/L.

If the mineral water is warm at the surface, has an annual mean temperature in excess of 25°C, it is termed thermal water. The thermal water which has proven curative effect is classified as medicinal water.

By their origin thermal waters can be classified according to the concentration ratio of minor ions [10]. The ratios of sodium (Na^+), calcium (Ca^{2+}) and

Table 1 Chemical compositions of the medicinal waters of Zalakaros and Margitsziget

Zalakaros		Margitsziget	
	mg dm^{-3}		mg dm^{-3}
K^+	58	K^+	43.4
Na^+	1810	Na^+	91.9
NH^+	12	Li^+	0.2
Ca^{2+}	136	NH_4^+	-
Mg^{2+}	47.5	Ca^{2+}	152.4
Fe^{2+}	0.15	Mg^{2+}	37.3
Mn^{2+}	-	Sr^{2+}	0.4
Cl^-	2420	Mn^{2+}	0.7
Br^-	6.5	Cl^-	122.9
J^-	5.4	Br^-	0.04
F^-	1.4	J^-	0.1
SO_4^{2-}	121	SO_4^{2-}	149.3
HCO_3^-	1650	HCO_3^-	507.5
S_{3-}^{2-}	2.9	COS	4.6
PO_4	0.12	SiO_2	37.4
HBO_2	155		
H_2SiO_3	19		
CO_2	733	CO_2	398.2
Total	7177.97	Total	1546.34

	Zalakaros		
	µg dm^{-3}		µg dm^{-3}
U	1.0	As	2.3
Ra_{226} (Bq cm^{-3})	22.1×10^{-4}	Rb	15
Th	0.5	Sr	4500
B	1000	Zr	8.1
Y	1900	Mo	5.2
P	46	Cd	2.5
Ti	0.8	Sn	2.2
V	0.24	Sb	2.9
Cr	2.7	Cs	1.0
Co	0.1	Ba	1400
Ni	5.4	W	3.3
Cu	37	Hg	0.5
Zn	15	Pb	2.9
		Bi	1.3

magnesium (Mg^{2+}), as well as chloride (Cl^-), a sulfate (SO_4^{2-}) and bicarbonate (HCO_3^-) assign 49 classes of thermal waters. If the mineral water contains a large amount of free carbon dioxide, it is termed acid water. Examples for such waters are thermal waters in Balf, Balatonfüred, Moha and Zalakaros. Waters rich in sulfide are thermal waters in Parád, Harkány and Margitsziget. Aperient waters contain either magnesium sulfate or sodium sulfate (Igmánd, Mira, Hunyadi János). Radioactive waters form a distinct category: their low radioactivity is not harmful for human health, on the contrary, they may be physiologically beneficial. The uranium and radon contents of the thermal water in Zalakaros exceed those of the lake in Hévíz, they are exceptionally high in the region. The exceptionally high concentrations indicate the presence of a granite strate below or near the mesosoic reservoir. This granite strate of 300 million years is on the surface at the Velence mountains in the Transdanubia. According to geological and hydrogeological studies the geothermal reservoirs of Zalakaros - Sávoly and Hévíz are on two different furrows in spite of their geographical proximity. The former is an open reservoir with replenishing potential.

The chemical compositions of the medicinal waters of Zalakaros and Margitsziget are compared in *Table 1.* As it can be seen in the table, the water in Margitsziget contains carbonyl sulfide. Károly Than was the first to identify this compound in medicinal water in 1871. COS is hydrolyzed to hydrogen sulfide and carbon dioxide. The presence of H_2S causes corrosion upon further treatment of the water. The medicinal water in Zalakaros has a total mineral concentration of nearly 7.2 g/L, predominated by sodium, chloride and bicarbonate. It also contains a multitude of trace constituents.

The depth of the well under study in Zalakaros is 2250 m. The temperature, pressure and total (carbonate) hardness at the bottom of the well is 121°C, 225 bar, 23.55°, respectively, the pH is 7.12. The temperature at the wellhead is reduced to 99.5°C, the pH is increased to 7.80 and total (carbonate) hardness drops to 10.88°. Upon the start of the well the daily output was 600 m^3 at a head pressure of 9 bar [4]. During our experiments the zero-point pressure was at a depth of 70 m. Currently the thermal water is pumped to the surface by the air lift exerted by the evolving gases (carbon dioxide and small amounts of H_2S).

Problems of operation

As it was described earlier, if the physical-chemical equilibria of the dissolved constituents are disturbed in the upwelling thermal water, precipitation occurs in the form of macro- or microcrystals. The microcrystals remain suspended in solution and pass through the wellhead, whereas the macrocrystals are deposited on the wall of the well tube and form a thickening layer of scale causing malfunctions in the operation of the well. Scaling is primarily caused by dissolved calcium and magnesium hydrogen carbonates responsible for the variable hardness of the water which, upon upwelling, are decomposed to insoluble calcium or magnesium carbonates, carbon dioxide and water. It should be noted that the starting point of precipitation is called critical or bubble point and is defined with its depth.

Recently scaling processes in the well tube was studied in details by Erika Kálmán and her co-workers [5, 6] in the case of the ternary system of $CaCO_3$ - H_2O - CO_2. They developed a computer model to study the kinetics of scaling. They emphasized that scaling and corrosion are inseparable problems during operation. They found, in harmony with others in the literature that the Langelier saturation index and Ryznar stability index can be used for the classification of scaling and corrosion in thermal waters of various compositions and temperatures. The more the measured pH differs from the saturation pH, the larger the tendency of the water for scaling and corrosion.

It is well known that dry and wet carbonic acid is capable of corroding steel and cast iron at higher temperatures, these materials are no longer corrosion-resistant at 100°C, nor are copper, lead and most plastics (e.g. PVC, PE, polystyrene, polyethylene, etc.). The structural material of the wells should be KO 33 stainless steel with austenite (Cr 19, Ni 9, C_{max} 0,07), or AISI 304 steel of similar composition, not only because they are highly corrosion- and erosion-proof, but also they have favorable temperature-strength characteristics. In addition, they can be connected to metallic and non-metallic structural materials.

Several procedures have been tried to prevent scaling in thermal wells.

Theoretically the ideal solution would be if the thermal well had a head pressure at which no or negligible amount of carbon dioxide was liberated so that precipitation was avoided. Such situation, however, rarely occurs in practice. The scale deposited can be removed chemically or mechanically. Both methods wear away the structural elements and have considerable cost-implications. Besides, temporal closing and restart of the operation may cause malfunctions. Inhibitors injected below the bubble point can also prevent scaling, but it is an expensive technology since large amounts of chemicals are needed and treatment of the extracted water may also be necessary. Researchers in the USA showed [7] that acidification prevented the precipitation of $CaCO_3$ and no corrosive products were deposited on the tube wall. In addition to the costs of the acid and its injection into the well a pH-regulator has to be installed. The pH of the water has always to be kept above 4, because at lower pH the rate of corrosion is significantly enhanced. Prior to any further utilization of the extracted acidic thermal water neutralization is needed.

In the early 80s in Zalakaros scaling was prevented by pressing degassed surface water below the bubble point into the well tube [4]. No scaling occurred when the thermal water was diluted by a factor of 2 or 3 with the injected tap water. The balneological use of the medicinal water of about 80°C did not require any further treatment, but large amounts of carbon dioxide were released into the atmosphere. For example, well A had a daily output of water and gas of 800 m^3 and 300 m^3, respectively, at deep-well B with an output of 600 m^3/d 15 m^3 gas was released for each m^3 of water. This and the increased cost of tap water called for the development of the system.

Experimental part

The objectives of the development were to ensure the smooth operation of the deep-well in Zalakaros, to fix the excess CO_2 evolving at a mass rate of 150 kg/h, and to produce new products or raw materials which contain dissolved salts in their natural ratio. The experiments were also aimed at determining the concentrations of trace elements in the products. Provided that the original trace element composition does not change, the product could be a potential medication.

It was the most straightforward to select $Ca(OH)_2$ for the fixation of carbon dioxide since Ca^{2+} cations were originally present in the thermal water. The absorption of CO_2 released from the wellhead in $Ca(OH)_2$ solution did not give good results. The excess base caused low precipitation efficiency and yielded $CaCO_3$ precipitate of highly variable quality. Therefore the calcium hydroxide suspension was injected into a mixing chamber installed below the bubble point. In the chamber all carbon dioxide is in the form of dissolved carbonic acid. Thus in the novel procedure quantitative precipitation occurs in the presence of excess acid, unlike precipitation in the presence of excess base. By keeping the proper rate of addition carbonate formation consumed about half of the carbon dioxide dissolved in the thermal water, before gas evolution had been started. At the bubble point the other half of the dissolved carbon dioxide evolved. It did not cause scaling but it was needed to exert air lift for the extraction of thermal water, i.e. to ensure the operation of the well.

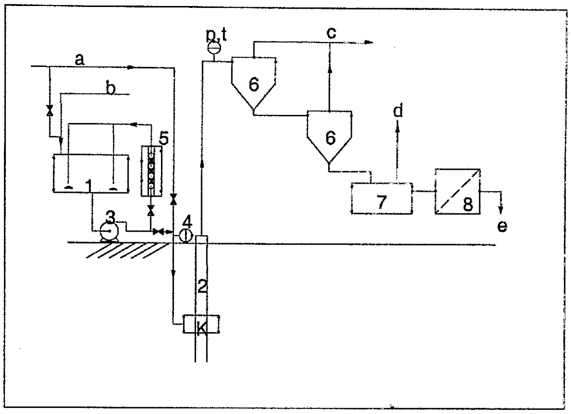

Fig.1 Flow chart of the new procedure
a./ diluent, b./ $Ca(OH)_2$, c./ gas, d./ product, e./ filtrate, k./ mixing chamber, 1./ homogenizer, 2./ well, 3./ pump, 4./ mass flow controller, 5./ static mixing tube, 6./ cyclone, 7./ centrifugal filter, 8./ filter press

The flow chart of the new process can be seen in *Fig.1.*

During the preliminary experiments water and $Ca(OH)_2$ suspension of technical quality were introduced into homogenizer 1. After the favorable results analytical grade $Ca(OH)_2$ suspension was used in the further experiments. Effective mixing was accomplished via recirculation driven by pump 3, in which the recycled fluid passed through the static mixing tube 5 [8] into the homogenizer stirred with hydrodynamical jet [9]. The $Ca(OH)_2$ suspension of 15 m/m % was then pressed into the mixing chamber K of well 2 at a depth of 400 m at a rate controlled by a mass flow controller 4.

The gas/liquid system exiting well 2 at a pressure *p* and temperature *t* flowed through the hydrocyclones 6. The separated gas was used in balneology, whereas the fluid was pumped through a centrifugal filter then through the framed filter press 8 for further treatment.

The filtrate was directly suitable for balneological use, whereas the precipitate from the centrifugal filter and the filter cake served as raw material for the production of new products.

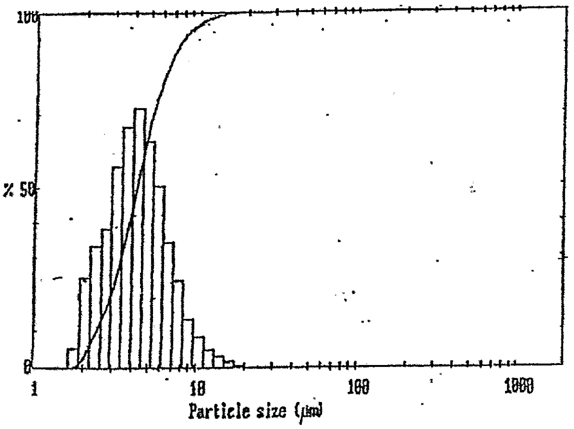

Fig.2 Flow sheet of the pressure of the well and the addition of $Ca(OH)_2$

Results

The efficiency of the removal of precipitate by the centrifugal filter was 75-80%. The remaining precipitate of 20-25% was effectively filtered with a framed filter press at low pressure drop and high filtration rate. The filtrate passed the mirror test so it can be returned to the well as a diluent. The degassed filtrate can replace tap water and can stabilize the chemical composition of the fluid in the well tube.

The grain size distribution of the filtered carbonate precipitate is shown in *Fig.2*. It can be seen in the figure that the maximum grain size is smaller than 20 µm, whereas the average grain size is 4 - 4,5 µm.

Figure 3 shows an example of variations of the pressure of the well and the addition of $Ca(OH)_2$ in time. The drop and increase of the pressure indicate the start and the end of the reaction, respectively. As it can be seen, the pressure was stabilized at a lower value about 10 minutes after the start. The addition of the suspension was ceased at 20 min. The reaction proceeded for some time and the well pressure returned to its initial value after about 30 min.

Discussion

The wet precipitate from the centrifugal filter contained about 50 % moisture by mass, in which all the ions originally present in the thermal water were dissolved.

An interesting feature of the novel technology is that when the fluid was expanded to atmospheric pressure and was evaporated to dryness, then crystallized thermonatrite (sodium carbonate) and halite (sodium chloride) were formed and the calcium carbonate was amorphous. It follows that in the technology the ratio of the trigonal lattice calcite, the orthorombic lattice aragonite and the amorphous calcium carbonate can be adjusted by varying the amount, concentration and temperature of the $Ca(OH)_2$ suspension injected into the mixing chamber of the well.

Other products can also be precipitated in various reactions (e.g. with H_2S) with the described technology in reactions with either dissolved ions or gas components. The experience gained with this new procedure can be used for economical and environmentally sound treatment of thermal waters from other, currently unexploited geothermal reservoirs.

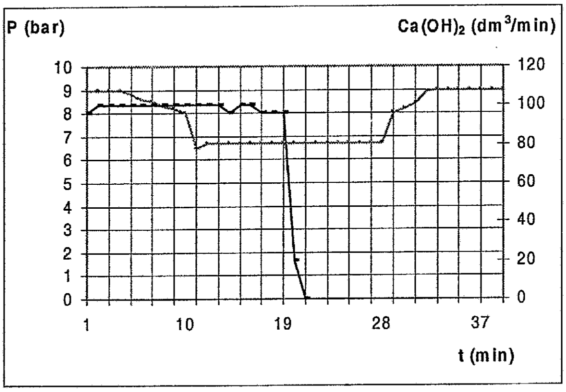

Fig.3 Grain size distribution of calcite crystals

Conclusion

To the best of our knowledge we were the first to successfully conduct a pilot-scale experiment in which $Ca(OH)_2$ reacted with carbon dioxide in the presence of excess carbonic acid. The initial acidity of the carbonate suspension quickly diminished under atmospheric conditions and the cooled precipitate and filtrate was found to be slightly basic. The precipitate recovered from the filters was loosely packed, pure calcium carbonate in the form of calcite microcrystals, containing halite in minor amounts. The adsorbed moisture retained the original ionic composition of the thermal water, except bicarbonate.

The reaction with $Ca(OH)_2$ did not affect the operation of the thermal well. Using this new procedure all constituents of the thermal water can be utilized in an environmentally sound manner.

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