Investigation of the Effects of Salinity and Temperature on the Removal of Iron from Water by Aeration, Filtration, and Coagulation

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Abstract

The use of geothermal water is becoming more and more popular for technological applications. But before this application water must be treated. Iron compounds cause precipitation of technical devices, which in turn reduces their efficiency. That is why we need to know how high temperatures and salinity effect water treatment. This paper determines the effectiveness of the iron removal process using four methods: aeration, aeration and filtration, aeration with coagulation, and coagulation, which were measured experimentally. The paper presents a procedure to optimize the coagulant dose and method of preparation of water model. Efficiency of iron removal was measured by the total iron concentration in raw and treated water model. It was shown that the effect of coagulation was the best method of iron removal with effectiveness up to 98-99.5%. Iron removal decreases with increasing salinity. Higher temperatures do not affect the process of iron removal in water.

Introduction

The growing interest in the use of geothermal water for technological purposes increases more and more its application [1]. The main limitation for its use has been high iron content in water. Iron compounds cause precipitation of technical devices, which often reduces their efficiency. The present literature knows little works dedicated to the influence of salinity on the process of iron removal. The method used for removing iron from water is coagulation [2, 3], where the following are most commonly used: iron salts (Fe) and aluminum (Al), such as aluminum sulfate $Al_2(SO_4)_3 \cdot 18H_2O$, ferric sulfate $Fe_2(SO_4)_3 \cdot 9H_2O$, etc.

What came to be used in the recent years were also other highly alkaline aluminum chlorohydrates, poly aluminum hydroxy chloro sulfates, poly aluminum chlorides, or zirconium oxides. These compounds are used as coagulants, hence they reduce the value of water quality indices such as color, turbidity, and oxidisability. Additionally, we note an increase in the effectiveness of pathogen removal, including protozoan cysts [4, 5]. In the pollution of surface waters, which are eliminated within the process of coagulation, it is the mineral compounds that cause turbidity and undissolved and dissolved organic compounds such as humic acids, planktonic microorganisms, and products of their metabolism [6]. Moreover, there is also an elevated concentration of iron in the groundwater. The use of traditional methods of treatment (aeration, sedimentation, and filtration) often are insufficient.

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Our study aimed to determine the effects of salinity on the process of removing iron from geothermal waters. This type of water salinity may appear high due to contact of the medium with rocks with a highly diverse composition. The weathering of basic magmatic and sedimentary rocks and the hydrolysis and oxidation of sulfide rocks into the waters result in iron ion penetration [7]. Before utilizing the water in heat exchangers or other geothermal installation elements, it must be treated.

One of the stages of treatment is the removal of iron ions from water. This element occurs most often in the form of iron (II) carbonate or iron (II) sulphate. In order to transform iron (II) form into insoluble and precipitating iron hydroxide $Fe(OH)_3$, the methods of aeration, liming, or coagulation are most commonly applied. Laboratory tests also recognize the effectiveness of three important methods of iron removal, namely on-air, filtration, and coagulation [8].

Suspended substances (colloids) are characterized by small size, high surface area, and a relatively large electric charge of the molecule. The destabilization of a colloidal system is often possible only by chemical treatment. Therefore, hydrolyzing aluminum salts are effective in removing contaminants and excess colloidal organic compounds [9]. The mechanism of the pre-hydrolyzed and coagulant hydrolyzing depends primarily on the polymeric forms of aluminum. With higher degrees of polymerization of aluminum, increasing a coagulant is able to neutralize electrokinetic potential contaminants present in the water. The consequence is a reduction in the required dose of coagulant [10].

Investigation Methodology

Solids are removed by sedimentation and filtration, where small particles such as colloids are not removed efficiently through sedimentation. Coagulation removes dirt and other particles suspended in water, as chemicals produce positive charges on the particles that can stick together. Alum and other chemicals are added to water to form tiny, sticky particles called "floc," which attract the dirt particles. Under the increasing weight of flocs, they become heavy enough to sink to the bottom during sedimentation. Coagulation by hydrolizing metal salts, typically of iron (Fe) or aluminium (Al), is the main reaction stage that drives the removal of natural organic matter and other contaminants in water treatment [4]. In the course of this investigation we have determined efficiency of iron removed with the use of alum coagulant against the aeration process. The efficiency of coagulation is influenced by certain factors such as pH, temperature, alkalinity, coagulant type, and mixing intensity. Many researchers have recommended a pH adjustment method to enhance coagulation efficiency. Another factor critical in the removal of turbidity is temperature [6, 11].

The forms of iron in the water not containing ligands depend on factors such as oxidation-reduction potential, pH, and total content of solids dissolved in water and tem-

Table 1. Doses salt water model.

Model water	NaCl	Na$_2$SO$_4$	FeSO$_4$
	[g/dm³]		
I	3	1	0.05
II	8	4	0.05
III	24	12	0.05
IV	100	50	0.05

perature (Fig. 1). In the course of further study it was essential to determine the parameters of model water, which was to be used in subsequent analysis.

Model Water Preparation

The aim of our study was to determine the effects of salinity on the process of removing iron from water with elevated temperatures, as in the case of geothermal water. Iron removal was based on the oxidation of Fe (II) to Fe (III), followed by removal of insoluble compounds by means of sedimentation or filtration. In order to compare the results of the studies, model water with different salinity was used.

Salts that have been used for this purpose were sodium chloride NaCl, sodium sulfate Na_2SO_4, and iron sulfate VI $FeSO_4$. Preparation of model water consisted of mixing with the use of a magnetic stirrer and 4-liter portions of distilled water with salt doses presented in Table 1 while maintaining equal content of ferrous sulphate $FeSO_4$ VI. As seen in Table 1, the amount of $FeSO_4$ is immutable, which provides a constant amount of Fe in each sample. The amount of other salts is changeable.
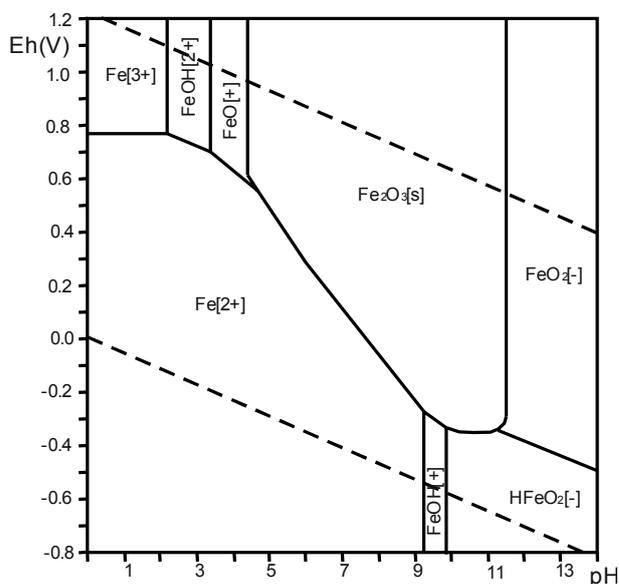

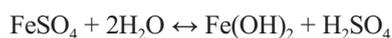Fig. 1. Eh-pH diagrams of the system Fe-O-H [Atlas of Eh-pH diagrams].

Table 2. Effect of pH on the removal of iron from the water for four different model waters.

	I salinity of water model: pH=6.84.after correction 7.01				II salinity of water model: pH=5.46.after correction 7.85				III salinity of water model: pH=6.41. after correction 6.95				IV salinity of water model: pH=5.34. after correction 7.34			
	Raw model water	Aeration and coagulation	Aeration	Coagulation	Raw model water	Aeration and coagulation	Aeration	Coagulation	Raw model water	Aeration and coagulation	Aeration	Coagulation	Raw model water	Aeration and coagulation	Aeration	Coagulation
pH	7.01	6.17	6.53	6.25	7.6	5.47	5.49	5.83	5.1	5.26	5.19	5.1	5.1	5.13	5.43	5.34
Electrolytic conductivity [mS/cm]	6.9	6.8	6.9	6.9	20	20.1	20	20	52.3	52.1	51.9	52	150.5	151.8	151.7	151.9
Total iron (decantation) [mg/dm³]	5.5	5.42	5.35	5.22	8.54	2.08	3.68	2.32	14.46	9.27	9.16	10	6.98	5.2	5.6	2.22
Total iron (filtrate) [mg/dm³]	5.42	5.4	5.28	4.96	0.1	0.05	0.05	0.05	3.96	4.01	3.98	3.97	1.94	2.21	2.21	2

Proper pH level influences the process of iron removal. In extreme cases the process can be terminated. The precipitation of sparingly soluble ferric hydroxide is possible when the following conditions are met:

- iron hydrolysis
- oxidation of Fe(II) to Fe(III)
- formation and agglomeration of particles of $Fe(OH)_3$
- removal of ferric hydroxide deposit

Hydrolysis of the ferric compounds is more intense at higher pH, thus requiring removal of the acidic reaction products. Carbon dioxide is removed by aeration and neutralizing the sulfuric acid alkalinity. Therefore, the alkalinity must be high enough to neutralize the acid formed by reacting [12]:

$$FeSO_4 + 2H_2O \leftrightarrow Fe(OH)_2 + H_2SO_4$$

and then:

1) $H_2SO_4 + NaOH \leftrightarrow Na_2SO_4 + 2H_2O$
2) $H_2SO_4 + Ca(OH)_2 \leftrightarrow CaSO_4 + 2H_2O$

After adding salts of strong acids, the pH of the water was dramatically reduced. It was necessary to raise the pH. Studies were conducted involving the addition of sodium hydroxide to raise the pH of the NaOH, and then the raw water was subjected to aeration process, coagulation, and aeration with coagulation. The results of the tests were shown that at a pH within a range of 7.9-8.1 we obtain the most efficient iron removal process. Furthermore, it was observed that the addition of NaOH resulted in the precipitation of iron $Fe(OH)_3$. We selected a few samples in order to determine a suitable pH of the water, i.e. one in which the precipitation of iron is possible (Table 2).

Determination of Coagulant Optimum Doses

The selection of the proper dose of coagulant is essential. For our research we selected coagulant produced by Enterprise Technical Services Dempol-Eco from Opole, Poland, having a trade name Flokor 1.2 A. This is an aqueous solution of aluminum hydroxychloride with a minimum pH of 4.2, an aluminum content of not less than 11%, and a chloride content of less than 7% [13]. This coagulant is used primarily for the treatment of liquid industrial wastes and municipal wastes and water treatment technology as well as in industrial applications. Determination of coagulant optimum dose was performed for the average values of salinity. The test results are given in Table 3.

All doses of coagulant reduce the iron content. Due to the very high salinity, it was decided to use the highest dose proposed, i.e. 50g/dm³, as appropriate for further studies.

Results

A water model was prepared initially in 4-liter beakers. Then the water was metered to four 1-liter beakers. Each liter of water was poured into four flasks, and was further subjected to a process of removing iron. In the first baker water was aerated for 30 minutes; in the second the water was aerated for 30 minutes and filtered on qualitative filter paper; the third contained coagulated water, and in the fourth was water subjected to aeration for 30 minutes, where coagulant was subsequently added.

Tests were carried out for the iron removal process at different temperatures in the range between 20ºC to 50ºC, where the temperature varied 5ºC. Hence the water was heated until the desired temperature was reached. The crafted water was heated in a water bath until reaching the desired temperature and subsequently cooled to room temperature. After cooling, it was subjected to deferrization with the use of the four different methods. The rapid mixing of coagulated samples lasted 2 minutes (200 ppm), and slow mixing lasted 15 minutes (30 ppm). For each method the sedimentation process lasted 60 minutes [14]. After this time the parameters were determined: pH with a pH meter, total iron with a spectrophotometer, and salinity (which is measured by conductivity) was determined using a conductivity meter.

Table 3. Coagulant doses for two types of salinity water model: II and III.

Coagulant doses		II salinity of water model: pH=7.92				III salinity of water model: pH =8.03			
		20 g/m³	30 g/m³	40 g/m³	50 g/m³	20 g/m³	30 g/m³	40 g/m³	50 g/m³
Supernatant liquor	Total iron [mg/dm³]	1.98	1.88	1.54	1.65	1.77	2.39	2.34	1.54
Filtrate		0.07	0.12	0.10	0.09	0.03	0.07	0.09	0.06
Supernatant liquor	pH	7.18	7.10	6.90	6.76	5.31	5.65	5.74	5.81
Filtrate		5.00	4.89	4.79	4.65	4.85	4.93	5.20	5.29
Electrolytic conductivity (supernatant liquor) [mS/dm³]		18.78	18.80	18.83	18.78	49.40	49.20	49.80	49.50

Fig. 2 depicts the effects of salinity on the efficiency of iron removal from the water, as measured by the total iron concentration of the following processes: coagulation, aeration, aeration with coagulation, and aeration with filtration. Fig. 2 shows that electrolytic conductivity, which is a measure of salinity, influences the removal of iron from water. Iron removal for all methods is positive. In the raw water, the total amount of iron was in the range of 6-13 mg Fe/dm³, and after purification attempts the amount of iron fell within 0.05-0.57 gFe/dm³, hence the effectiveness rose up to 95-99.5%. The maximum removal of iron reached from 12.20 mg Fe/dm³ to 0.05 mg Fe/dm³. The effectiveness of the process decreases with increasing salinity. The most effective method of reducing the compounds of iron is coagulation. Tests with aeration did not produce such a high efficiency. It has been observed that the process of aeration causes good precipitation of iron. However, in combination with other methods it aggravates the results. Therefore, aeration is not recommended when removing iron within other methods.

Fig. 3 presents the effect of temperature on the efficiency of iron removal from the water, as measured by the total iron concentration of the following processes: coagulation, aeration, aeration with coagulation and aeration with filtration. Each point on the graph is the arithmetic mean of four measurements for the following methods: coagulation, aeration, aeration with coagulation and aeration with filtration. There is no clear correlation between water heating and iron removal efficiency on the water.

At this stage of the study there was no significant effect of the temperature limiter on the iron removal effi-
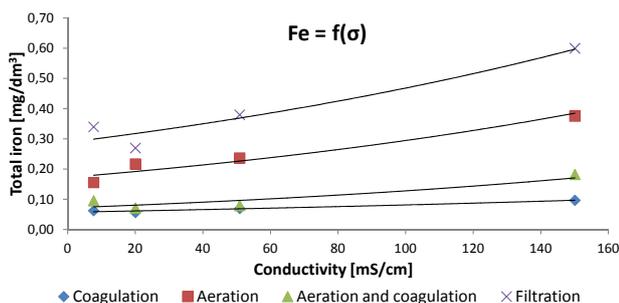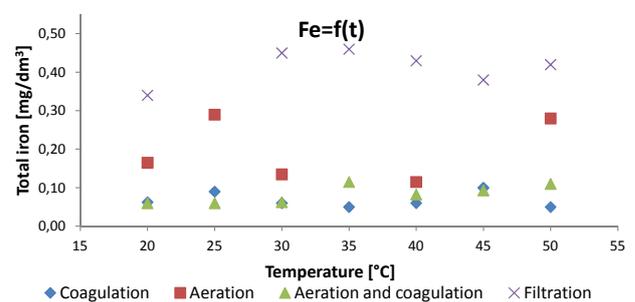

Fig. 3. Effect of temperature on the efficiency of iron removal from water.

ciency, although the studies on low-mineralized geothermal water intake in Zawada near Opole [15], clearly showed a correlation between water temperature and the solubility of iron compounds [7]. The increase of water temperature causes an increase in the solubility of iron compounds. In turn, the higher the solubility of iron compounds conversely affects the iron removal process. The most effective method of reducing the compounds of iron resulted in coagulation. Tests with aeration did not produce nearly high efficiency.

Conclusion

The effectiveness of the iron removing process decreases with increasing salinity. Total iron content in raw water was in the range of 6-12 mg Fe/dm³, but after filtration the amount of iron fell within 0.30-0.57 mg Fe/dm³ (effectiveness 92.2-96.4%). After aeration the amount of total iron was within 0.15-0.30 mg Fe/dm³ (effectiveness 96.2-98.1%), and after aeration and coagulation iron content was within 0.05-0.15 mg Fe/dm³ (effectiveness 98.4-99.3%). After coagulation the amount of iron fell within 0.05-0.10 mg Fe/dm³ (effectiveness 98.7-99.4%). The most effective method of reducing the compounds of iron is coagulation. Tests with aeration did not produce such a high efficiency. Due to the composition of the water model treatment process, the salting-out effect is in competition with the adsorption of the anions Cl- iron hydroxide on the surface, thus impeding coagulation and filtration.

Fig. 2. Effects of salinity on the efficiency of iron removal from water.

Heating the water to a desired temperature and then cooling it down does not affect the process of iron removal in water. The most effective method for reducing the compounds of iron is coagulation. Tests with aeration did not produce such a high efficiency. Therefore, the august deferrization can be applied irrespectively in the technological system.

The addition of a coagulant gives positive results in removing iron from water. It is effective despite high salinity and high temperatures.

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