Journal of Chemical Technology and Metallurgy, 54, 5, 2019, 993-998

THE ESTIMATION OF THE EFFICIENCY OF MINE WATER STABILIZATION TREATMENT METHODS DURING EVAPORATION (M. GORKY MINE, DONETSK C.)

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Received 08 October 2018
Accepted 12 April 2019

ABSTRACT

This paper presents the results of research on the efficiency of reagents for mine water stabilization depending on the conditions of their application, characteristics, type and added amount of the reagents. Estimation of the efficiency of stabilizers of the scale formation was determined using heat-electric heaters. The water hardness was determined by titrimetric methods. The stabilizer of scale formation SMDS was synthesized from paraformaldehyde and sodium hydrosulfite. Efficiency in relation to scale formation was determined by investigation of water stabilization from the M. Gorky mine.

The research showed that phosphonic-acids based stabilizers (OEDPA, NTMPA) were the most effective ones. The new highly effective SMDS scale formation stabilizer was proved to be not inferior to phosphonic acids and created a stabilizing effect on 100 % level.

A new developed scale formation stabilizer allowed efficient use of water in cooling and heat supply systems. It should be noted that efficiency of SMDS is not inferior to organic acids. Created compositions on the basis of phosphonates, sulfonates and sulfuric acid provided a high resistance to deposit formation in mine waters with hardness up to 14 mg-eq/dm^3, at that concentration of sulfuric acid did not exceed 2 - 3 mg-eq/dm^3, the dose of the stabilizer was < 5 mg/dm^3. The resulting scale formation stabilizer for water-cycle cooling and heat supply systems on the basis of affordable, cheap raw materials will increase the efficiency of the heat-exchange equipment, reduce water discharges for blowdown. It will allow wide introduction of closed water-circulation systems that will increase the level of environmental safety of heat supply and will significantly reduce water consumption in industry and power sector without significant reconstruction of water conditioning and water purification stations.

Keywords: stabilization effect, evaporation coefficient, scale formation inhibitor.

INTRODUCTION

It is known that the largest volume of water are used in heat exchange equipment to remove excessive heat. In working conditions of circulation systems, heating of water up to 40 - 45ºC and cooling it in cooling towers or splashing basins multiple times leads to the losses of carbon dioxide and formation of deposits of calcium carbonate on surfaces of heat exchangers and pipes [1]. In heat exchange equipment, phosphonic compounds (phosphonates) are being used more and more often as an alternative to water softening. To extend the area of effective use of phosphonates, scientists have created a CCF composition, which is suitable for prevention of both scale formation and corrosion in heat exchange systems [2]. The base of the CCF composition is made from domestic reagents, is multicomponent and consists of phosphonic acids, its phosphonic and synergistic additives of organic and inorganic substances. Experimental industrial tests of the CCF in closed heat-exchange systems with NR-18 and NR-20 low-power boilers and temperature mode 70 - 95ºC with the addition of a hard (23 mg-eq/kg), non-aerated water were conducted by the authors. In all cases, positive results were obtained. The CCF is not only an effective suppression for the carbonate, sulphate, silicate and iron-oxide scale, but also inhibits corrosion at the same time.

The problem of mineral salts deposition on the surface of heat exchangers was considered by authors [3]. In order to inhibit the process of fouling, the addition of a mixture of the following phosphonates to the circulation water was proposed: 1-hydroxyethylene-1,1-diphosphonic and diethylenetriampinate ethylenphosphonic acids. It was noticed that composition of these reagents has synergistic effect. The typical concentration of the composition is 25 mg/dm^3.

The purpose of this work was to study the processes of scale formation, determination of the effectiveness of reagents for water stabilization depending on conditions of its use, characteristics, type and dose of reagents.

EXPERIMENTAL

Materials and methods

Alongside with known inhibitors of scale formation and metal corrosion based on phosphonic acids and polyphosphates, the new highly effective sodium methyldisulfonate stabilizer (SMDS) was synthesized, that, as other known inhibitors, was capable of creating thermodynamically stable 6-membered cycles and provided high water stability in sediment formation [4, 5]. It is important because nowadays the main disadvantages of phosphonate-based inhibitors are their high cost and the difficulty to obtain.

For the synthesis of SMDS (sodium methylenedisulfonate), paraform and sodium hydrosulfite were used:

$$2NaHSO_3 + CH_2O \rightarrow CH_2(SO_3Na)_2$$

For the preliminary assessment of the efficiency of water stabilizers in relation to the scale deposits formation, different studies were conducted to stabilize water from M. Gorky mine.

The process of scale formation was studied at 80°C. Such conditions of the process allow estimating stabilizers at a relatively small period of heating of the solution - 6 hours. The volume of the solution used was 100 cm^3.

The residual hardness of water in the samples was determined by complexometric titration with eriochrome black T as an indicator [6].

Stabilizing effect (SE) in this case was calculated by the decrease of hardness of the solution due to heating:

$$SE = \left(1 - \frac{\Delta Hi}{\Delta H}\right) 100\ \%$$

where:

ΔH - reduction of hardness of the solution treated with the inhibitor,

ΔH - reduction of hardness of the initial solution.

RESULTS AND DISCUSSION

The problem of calcium sulfate solutions stabilization is critical for Donbass industrial and power engineering facilities. Unlike the most regions of Ukraine, where water has low mineralization and calcium carbonate hardness, rivers in Donbass and Pryazovya have high mineralization and calcium carbonate hardness because of mine and industrial wastewaters discharge as well as the presence of natural phosphates [7]. The acidic water stabilization treatment leads to bicarbonates displacement and rising of calcium sulfate level. This method is effective with low mineralized water. In case of high mineralization, the problem of calcium sulfate sediments on heating equipment appears. That is why it makes sense to use scale formation inhibitors.

In this research work we used the synthesized sodium methyldisulfonate (SMDS), and also oxyethylidenediphosphonic acid (OEDPA) and nitrotrimethylphosphonic acid (NTMPA) for the comparison. Almost all compositions, which nowadays are used as scale formation inhibitors in the power engineering and industry, were created on the basis of the last three compounds.

It should be admitted that evaporation processes make a great impact on water stability and inhibitors efficiency. That is why water was heated at 40°C up to the evaporation coefficient $E_c \approx 1.5$ to estimate the efficiency of reagents in conditions same as in water circulation systems. The results can be seen in Tables 1 and 2.

To sum up, in this case an absolute water stability can be reached at 2 mg/dm^3 dose of SMDS inhibitor, 5 mg/dm^3 of phosphonic acids, and the dose of phosphonic acids can be decreased to 2 mg/dm^3 when using sulfuric acid [8].

Table 1. Stabilizing effect (SE) dependence on the type and dose of reagents while heating water from M. Gorky mine ($t = 40°C$, $H = 14,4$ mg-eqv/dm^3).

Reagent	Dose, mg/dm^3	Evaporation coefficient, E_c	H_f, mg-eqv/dm^3	H_i, mg-eqv/dm^3	ΔH, mg-eqv/dm^3	SE, %
—	—	1,57	14,4	20,9	6,3	—
OEDPA	2	1,69	18,1	20,9	2,8	55,5
	5	1,43	17,9	17,9	0,0	100,0
NTMPA	2	1,49	17,4	18,6	1,2	81,0
	5	1,57	19,6	19,6	0,0	100,0
SMDS	2	1,52	18,7	18,9	0,2	96,8
	5	1,55	18,4	18,4	0,0	100,0
H_2SO_4; OEDPA	98; 2	1,51	18,7	18,9	0,2	96,8
	98; 5	1,49	18,6	18,6	0,0	100,0
	245; 2	1,49	18,6	18,6	0,0	100,0
	245; 5	1,56	19,5	19,5	0,0	100,0
H_2SO_4; NTMPA	98; 2	1,49	18,5	18,6	0,1	98,4
	98; 5	1,45	18,1	18,1	0,0	100,0
	245; 2	1,63	20,4	20,4	0,0	100,0
H_2SO_4; SMDS	98; 2	1,52	19,0	19,0	0,0	100,0
	98; 5	1,56	19,5	19,5	0,0	100,0
	245; 2	1,56	19,5	19,5	0,0	100,0

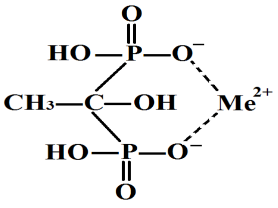
In the previous experiments sulfuric acid was used in concentrations about 2 - 5 mg-eqv/dm^3 (98 - 245 mg/dm^3). It was interesting to check water stability while using lower concentration of sulfuric acid and adding phosphonic acids - OEDPA and NTMPA, as well as SMDS inhibitor. The results are presented in Table 3.

In this case with the simultaneous application of phosphonic acids and sulfuric acid, full water stability can be achieved, while the consumption of both sulfuric acid and phosphonic acids being reduced significantly. The efficiency of OEDPA almost did not differ from the efficiency of NTMPA. SMDS synthesized by the authors is not inferior in efficiency to the more known scale formation stabilizers based on phosphonic acids and is much cheaper.

At the doses of SMDS 2 mg/dm^3 and sulfuric acid 25 mg/dm^3 and higher, there was a stabilization effect at the level of 100 %, which proved the efficiency of this inhibitor.

High efficiency of phosphonic acids is ensured due to the formation of persistent chelate structures. The OEDPA molecule is capable of creating six-membered chelate complexes with hardness-ions, which are thermodynamically favorable and stable.

The structure of the OEDPA complex with hardness-ions is:



where: $Me^{2+} - Ca^{2+}, Mg^{2+}$.

Table 2. Influence of the type and dosing of the reagents on the water stability (M. Gorky mine) related to scale formation (t = 98°C, T = 6 hours, $E_s = 1$, H =12,5 mg-eqv/dm^3).

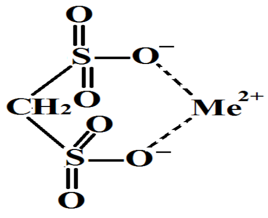
Reagent	Dose, mg/dm^3	H_i, mg-eq/dm^3	ΔH, mg-eq/dm^3	SE, %
———	——	7,9	4,6	0,0
OEDPA	1,0	7,9	4,6	0,0
	2,0	9,6	2,9	37,0
	5,0	11,6	0,9	80,4
	10,0	12,0	0,5	89,1
NTMPA	1,0	8,0	4,5	2,2
	2,0	9,3	3,2	30,4
	5,0	11,7	0,8	82,6
	10,0	12,2	0,3	93,5
SMDS	1,0	10,1	2,4	48,0
	2,0	12,5	0,0	100,0
	5,0	12,5	0,0	100,0
	10,0	12,5	0,0	100,0
H_2SO_4; SMDS	98; 1	10,8	1,7	63,0
	98; 2	12,5	0,0	100,0
	98; 5	12,5	0,0	100,0
	98; 10	12,5	0,0	100,0
	148; 2	12,5	0,0	100,0
	245; 2	12,5	0,0	100,0
H_2SO_4; OEDPA	98; 1	11,9	0,6	87,0
	98; 2	12,2	0,3	93,5
	98; 5	12,5	0,0	100,0
	98; 10	12,5	0,0	100,0
	148; 2	12,5	0,0	100,0
	245; 2	12,5	0,0	100,0
H_2SO_4; NTMPA	98; 1	12,0	0,5	89,1
	98; 2	12,1	0,4	95,8
	98; 5	12,5	0,0	100,0
	98; 10	12,5	0,0	100,0
	148; 2	12,5	0,0	100,0
	245; 2	12,5	0,0	100,0

Table 3. The influence of reagents on water stability (M. Gorky mine (t = 40 °C, H = 14,3 mg-eqv/dm^3).

Reagent	Dose, mg/dm^3	Evaporation coefficient, E_c	H_f, mg-eqv/dm^3	H_i, mg-eqv/dm^3	ΔH, mg-eqv/dm^3	SE, %
—	—	1,39	12,10	18,63	6,53	—
H_2SO_4; SMDS	25; 1	1,47	15,4	21,46	6,06	7,2
	49; 1	1,43	19,8	20,90	1,10	83,2
	74; 1	1,49	19,9	21,80	1,90	70,9
	25; 2	1,49	21,9	21,80	0,00	100,0
	49; 2	1,51	22,0	22,00	0,00	100,0
	74; 2	1,50	21,9	21,90	0,00	100,0
H_2SO_4; OEDPA	25; 1	1,40	14,2	15,00	1,20	82,0
	49; 1	1,45	16,0	17,30	1,30	80,0
	74; 1	1,43	18,2	19,60	1,40	79,0
	25; 2	1,50	19,2	20,00	1,20	82,0
	49; 2	1,50	21,3	21,60	1,30	80,0
	74; 2	1,49	21,7	21,70	0,00	100,0

This causes the formation of stable compounds of OEDPA and hardness-ions when micro-crystals are formed from calcium carbonate or magnesium hydroxide. The inclusion of branched OEDPA-anions in the crystals breaks their symmetry and prevents their growth. Therefore, small micro-crystals do not settle down on heat-exchange surface, but are being removed with water from the heat transfer zone.

The SMDS molecules, like the OEDPA molecules, are capable of the formation six-membered cycles. Exactly these structural features can explain the high efficiency of this inhibitor at mine water stabilization.



where: Me^{2+}– Ca^{2+}, Mg^{2+}.

CONCLUSIONS

The conditions of protecting the heating equipment from scale formation in the mineralized waters during evaporation were determined. The most effective stabilizers were phosphonic-acids based ones - OEDPA, NTMPA.

A new high-performance sulphonate stabilizer SMDS was sintesized, which was capable of formation of thermodynamic stable 6-member cycles, as well as other more well-known stabilizers, and provided high stability of water in relation to mineral deposits formation.

It was found that combined treatment of water by acid and scale formation stabilizers was more promising. With the combined treatment of the mine water by sulfuric acid and SMDS, high levels of water stability were achieved with 1 - 2 mg-eq/dm^3 acid consumption and 1 - 2 mg/dm^3 stabilizer doses.

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