

Application of S-HGMS and chemical coupling technology in river water treatment

Xin Zhao, Su-qin Li*, Shuai-shuai Han, Peng Zhang, Jian-jiang Jin, and Peng-hui Guo

School of Metallurgical and Ecological Engineering, University of Science and Technology Beijing, Beijing 100083, China

(Received 7 November 2019; revised or reviewed 27 June 2020; accepted 28 June 2020)

Abstract

Circulating cooling systems consume a lot of water, and most of the water from river, which contains a large amount of Ca²⁺, Mg²⁺, et al, and has the characteristics of high hardness and large turbidity. The water can form scale on the surface of the heat exchanger and the pipes, which would reduce the heat transfer efficiency and affect the heat exchanger's length of service. In this study, the Superconducting High Gradient Magnetic Separation (S-HGMS) technology was used in river water treatment and the effects of agent A, agent B, and S-HGMS on the removal of hardness and turbidity were discussed. The results showed that the hardness removal rate reached 71.3% and the turbidity was decreased to 0.5 NTU.

Keywords: S-HGMS, river water, removal of hardness and turbidity, scale inhibition

1. INTRODUCTION

Water is often used for equipment cooling in steel and power companies, and the safe operation of the equipment is closely related to the quality of cooling water. The amount of cooling water is very large, which accounts for 60%-80% of the total industrial water [1-2]. It is often subjected to wind, splashes, evaporation and other effects during the operation of circulating cooling system, so water must be continuously replenished. The concentration of ions increases with increasing cycle of concentration if the quality of the circulating water is not good, which will result in damage to the circulation system and even cause industrial accidents.

River water is generally used as the make-up water in circulating cooling system and it is a high hardness water which has high concentration of calcium and magnesium ions [3-4]. River water contains a lot of impurities which would form scale on the heat exchanger and the surface of the pipes when used directly [5]. Scale has many disadvantages, such as blocking pipes, reducing heat transfer efficiency, causing corrosion of pipes, et al.

At present, most enterprises adopt the traditional chemical methods to prevent scaling, use lime or sodium carbonate to precipitate scaling, or add chemical inhibitors or use ion exchange method to replace scaling with soluble ions. These methods are effective, but they are expensive and would change the chemical property of water. Therefore, various physical methods are invented to substitute chemical water treatment methods in order to avoid their doing harm to the environment and the health of human. S-HGMS technology, which is an emerging magnetic processing technology, is mainly used for the

screening of magnetic materials [6-8]. With the development of researches, S-HGMS technology has been applied to the water treatment in recent years [9-11]. This technology produces high gradients field with a magnetic device [12].

Flocculation technology is widely used in the deep treatment of wastewater [13]. The river water contains a large number of colloids and suspended substances. Due to the fact that the gravity is less than the buoyancy, these substances are not easy to precipitate. Flocculant has the function of coagulation, which could make these substances become large flocs and finally form precipitates.

In this study, agent A was an inorganic chemical agent that could make Ca²⁺ and Mg²⁺ become precipitate and separate them out of the water. Agent B was an inorganic high-efficiency composite flocculant that accelerates the precipitation of flocs in water. S-HGMS technology combined agent A with agent B to treat the river water. The effects of agent A, agent B, and S-HGMS on the hardness and turbidity of river water were studied.

2. MATERIALS AND METHODS

2.1. Materials

The raw water for the experiment was taken from the Fuyang River in Handan, China, and was mainly used to make-up water in the circulation system of Handan Iron and Steel Group. Fuyang River water was high-hardness, high-alkalinity, and multi-impurity source water. It would form scale and damage the cooling system if they were directly used as the make-up water in circulating water system. The water sample was taken from the inlet of the make-up water system, and the scale of the water quality analysis is shown in Table 1.

* Corresponding author: lisuqin@metall.ustb.edu.cn

TABLE 1
ANALYSIS RESULTS OF RAW WATER

Water quality index	Unit	Value
pH	-	7.22
Turbidity	NTU	7-10
Hardness	mg/L	400-500
Alkalinity	mg/L	265
SS	mg/L	40-100
SiO ₂	mg/L	28.8
Fe	mg/L	0.6
Cl ⁻	mg/L	83
SO ₄ ²⁻	mg/L	257.4
NO ₃ ⁻	mg/L	6
COD	mg/L	4.72
BOD	mg/L	3.62
Conductivity	us/cm	1200

TABLE 2
XRF ANALYSIS OF SCALE IN CIRCULATING COOLING SYSTEM.

Element	Content (%)	Element	Content (%)
Ca	46.31	Zn	2.63
O	34.40	S	1.41
Mg	4.94	Fe	1.34
Si	3.37	Na	0.62
P	3.37	Al	0.49

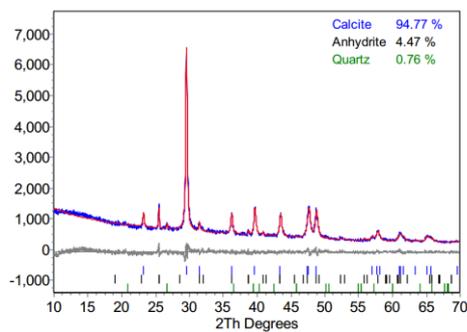


Fig.1. XEM analysis of scale.

2.2. Analysis of scale

In order to research the influence of water quality on cooling system, some scales were collected on the surface of condensation pipes. It was a composite scale which contained calcium, magnesium, silicon, zinc, et al. The results of XRF analysis are shown in Table 2. With XRD analysis, the scale was mainly composed of calcite, anhydrite and quartz. The results are shown in Fig.1. In order to avoid the formation of scale, the removal of Ca²⁺ and Mg²⁺ was necessary.

2.3.. Experimental system

The experimental device of S-HGMS was produced by the Institute of High Energy Physics of Chinese Academy of Sciences. S-HGMS equipment parameters are shown in

TABLE 3
THE PARAMETERS OF S-HGMS.

Magnetic flux	0~5.5 T
Magnetic field gradient	20 T/m
Magnetic field aperture	200 mm
Equipment height	1520 mm
Outer diameter of equipment	1480 mm
Weight	9 t
Working temperature	4.2 K
Power consumption	8 kW

Table 3. Firstly, the optimal addition amount of agent A and agent B were studied. The river water was brought into the agitating vessel by peristaltic pump and agent A was added into it at the same time. When the water entered the flocculation device through peristaltic pump, and agent B was added. Finally, the water entered S-HGMS system, most hardness and turbidity were removed. The process chart is shown in Fig. 2.

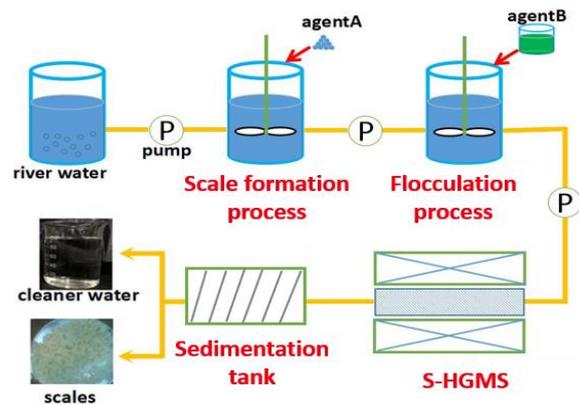


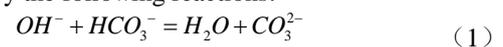
Fig. 2. Process chart of S-HGMS and chemical coupling treatment of river water.

3. RESULTS AND DISSCUSSION

3.1. Effect of agent A on hardness

The hardness of river water declined with the addition of agent A. It gradually tended to a fixed value which maintained at about 120 mg/L when the amount of agent A was 300 mg/L. Then, the hardness removal rate was up to 71.3%, the results are shown in Fig.3.

The reason was that with the addition of agent A, HCO₃⁻ in the river water reacted with OH⁻ to form CO₃²⁻. CO₃²⁻ reacted with Ca²⁺ to form CaCO₃, which was a kind of precipitate; Mg²⁺ reacts with OH⁻ to form Mg(OH)₂, which was a slightly soluble substance. It could be explained by the following reactions:



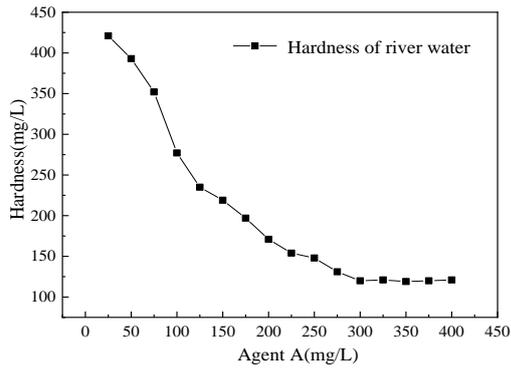
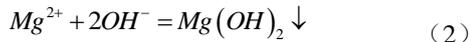


Fig. 3. The effect of agent A on hardness.



Both Ca^{2+} and Mg^{2+} were completely reacted when the amount of agent A is 300 mg/L, so the hardness remained substantially unchanged when agent A was continuously added.

The hardness of water included temporary hardness and permanent hardness. Temporary hardness was mainly carbonate and bicarbonate. Agent A could react with bicarbonate to form CaCO_3 and $\text{Mg}(\text{OH})_2$, thus reduced the temporary hardness. However, the water also contained SO_4^{2-} , NO_3^- , Cl^- and so on. The compounds formed by the combination of these ions and Ca^{2+} and Mg^{2+} mainly exist in the form of sulfate, nitrate and chloride, which were called permanent hardness and would exist in the water permanently. The hardness no longer changed when the dosage of agent A was 300mg/L. It meant that agent A reacted with bicarbonate to form CaCO_3 and $\text{Mg}(\text{OH})_2$ and the temporary hardness was removed.

3.2. Effect of agent B on turbidity

Added agent B into the river water when the scale formation process was finished. Firstly, set up stirring speed as 300r/min, 1min, respectively. Secondly, adjusted the stirring speed as 100r/min, 10mins, respectively. Finally, measured the turbidity of supernatant after 4 mins. The result is shown in Fig.4. Flocs volume and quantity increase with the addition of agent B, and the flocculation sedimentation rate was best when the amount of agent B was 50 mg/L.

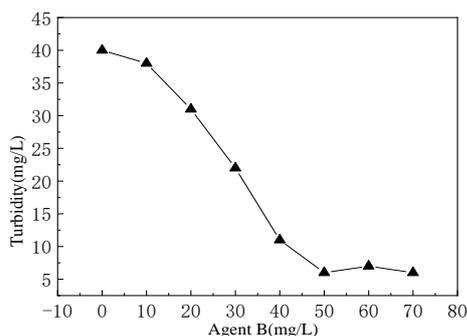
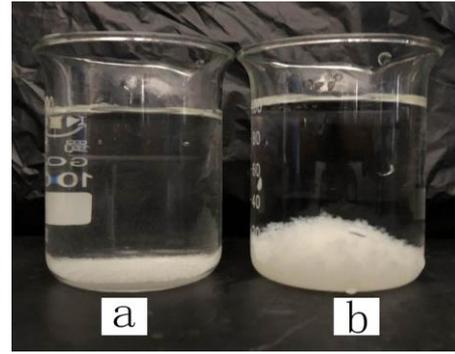


Fig. 4. The effect of agent B on turbidity.



a: Untreated by S-HGMS b: Treated by S-HGMS

Fig. 5. Effect of S-HGMS treatment on scale.

When a certain amount of agent A was added into the river water, a suspension of CaCO_3 and $\text{Mg}(\text{OH})_2$ was formed and the turbidity of the water is increased. Agent B is quickly mixed with the suspension and react when it was added into water. Agent B had much stronger adsorption and capture capabilities than others. Suspended solids collide with each other and formed large flocs during the agitation process and finally precipitate.

3.3. Effect of S-HGMS on scale

The flow rate was 500r/min, magnetic flux density and treatment time were 3T, 30 mins, respectively; the dosage of agent A and agent B were 300 mg/L, 50 mg/L, respectively. Water passes through the S-HGMS device under the above conditions. Compared with untreated, the flocs become loose and the appearance structure changes after HGMS treatment, the results are shown in Figure 5.

Flocs formed were analyzed after adding agent A, adding agent B and S-HGMS, respectively. The result is shown in Fig.6. Fig.6(a) was the SEM of flocs after added agent A. It could be seen that the flocs were in the form of solid bodies, which were loosely gathered together. These cubic particles were CaCO_3 and $\text{Mg}(\text{OH})_2$ formed by Ca^{2+} and Mg^{2+} . Due to the irregular shape and small volume, the particles present a relatively stable state in the water. Suspended solids and colloids could not settle by their own gravity. Fig.6 (b) was the SEM of the flocs after added agent B. Agent B was a high-efficiency composite flocculant, which was spherical or elliptical in shape, and had a good coagulation effect. It could make small flocs stick together tightly, formed a large and compact flocs. Agent B had a branch like structure. Because of this structure, suspended solids, colloids and flocculant hydrolysates were linked together to form flocs. The flocs would not be damaged due to agitation and had strong stability. Fig.6(c) was SEM of floccules at the bottom of inclined plate sedimentation tank after S-HGMS treatment. S-HGMS treatment destroyed the stability between the floc particles and water molecules. The colloid had different charge and movement was accelerated under the action of S-HGMS. The colloid takes CaCO_3 and $\text{Mg}(\text{OH})_2$ as the center to form flocs.

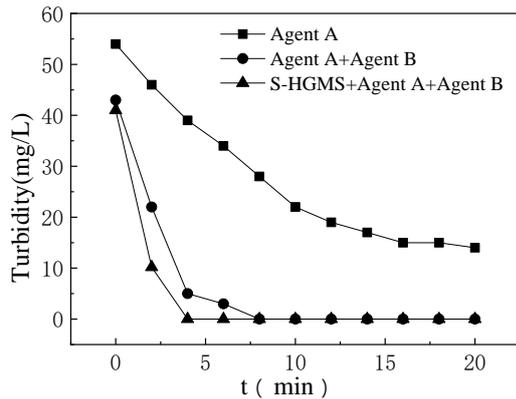


Fig. 7. Effect of different methods on turbidity.

The flocs accelerate the collision and become larger, thus strengthening the effect of chemical flocculation. The flocs were aggregated and precipitated by HGMS and flocculation.

3.4. Effect of S-HGMS on turbidity

The effects of agent A, agent B and S-HGMS on turbidity were studied and the result is shown in Fig. 7. In order to better shown the effect of agent A, agent B and S-HGMS, the water sample was divided into three equal parts. The first water sample added agent A, and the second water sample added agent A and agent B. The third water sample added agent A and agent B, and the water sample was processed by S-HGMS. After the same agitation, S-HGMS treatment had the fastest settling speed of flocs, and the flocs were relatively loose. The change rate of turbidity was much higher than that of the untreated one and the turbidity decreased to below 0.5 NTU. S-HGMS treatment could destroy the stability between particles and water molecules. Different charged particles adsorbed and aggregated each other and flocculated around CaCO_3 or Mg(OH)_2 . Agent B could accelerate the flocculation of particles and form large number of flocs. Under the action of double flocculation, the flocs in water precipitated rapidly.

3.5. Effect of S-HGMS and possible mechanism

It is currently believed that magneto-hydrodynamic is the mechanism involved in magnetized water treatment. In the mechanism of magneto-hydrodynamic, the Lorentz force is important to generate magneto hydrodynamic effects. It showed the effects of the dynamic magnetic

treatment as the consequences of the action from the Lorentz force [14]. Lorentz force is generated when charged particles moving through the magnetic field. The magnitude of this force is defined as follows:

$$|F_L| = q|v \times B| = qvB \sin \theta$$

where, F_L is the Lorentz force, q is the quantity of charged species, v is the velocity of particles, B is the magnetic field, and θ is the angle between v and B vectors.

This force is related to particle charge, particle velocity and magnetic field strength. Magnetic field produces a force on the fluid by processing the flowing solution [15]. The particles in the river water gain kinetic energy to a certain extent. The freely moving particles collide with each other at a higher rate, and more particles will precipitate together. Therefore, the solution flocculation speed was accelerated after S-HGMS treatment, as shown in Fig 7. The magnetic field neutralized the surface of particles and causes shifting of ions from the bulk solution towards the particle surface, which can affect crystallization and aggregation processes [16]. Therefore, this phenomenon accelerates the coagulation of scale forming particles during and after S-HGMS treatment. In this context, the coagulation rate was increased by increasing the magnetic flux density and the flow velocity through the magnetic. In this study, the flow rate of 500 r/min and the magnetic flux density of 3T were the best. The collision speed between the particles increases, and attraction is generated between the opposite charged particles, so the particles eventually gather together. Under the combined action of S-HGMS and flocculant, the flocculation was accelerated.

4. CONCLUSIONS

S-HGMS could accelerate flocculation and sedimentation of particles. The results showed that hardness and turbidity of raw water were decreased with the S-HGMS treatment after adding agent A and agent B. The precipitation was loose and not easy to adhere on the inner surface of pipe.

After S-HGMS treatment, the hardness removal rate was up to 71.3% and the turbidity was below 0.5NTU.

S-HGMS technology had advantages of low investment, energy saving, simple operation and automatic control, and had a good application prospect.

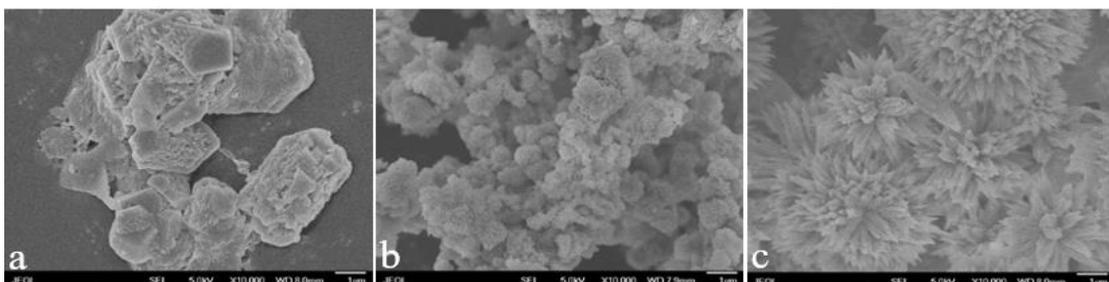


Fig. 6. SEM of flocs. a: adding agent A; b: adding agent B; c: S-HGMS

ACKNOWLEDGEMENTS

This work was financially supported by Major Science and Technology Program for Water Pollution Control and Treatment (grant no. 2017ZX07402001). The authors thanks Zian Zhu, and Guoqing Zhang from Institute of High Energy Physics, Chinese Academy of Sciences for their assistance.

REFERENCES

- [1] Y. B. Jin, "Discussion on Energy-saving Eesign of Circulating Cooling Water System in Iron and Steel Enterprises," *Metallurgical Energy*, vol. 28, no. 01, pp. 49-52, 2009.
- [2] M. N, M. F, A. Y, et al., "Removal of Iron Oxide With Superconducting Magnet High Gradient Magnetic Separation from Feed-Water in Thermal Plant," *Transactions on Applied Superconductivity*, vol. 25, no. 3, 2015.
- [3] X. Y. Huang and J. Z. Lu, "High Hardness, High Alkalinity and High Chlorine Circulation Water Treatment," *Petrochemical Industry Application*, vol. 05, pp. 82-85, 2008.
- [4] X. Z. Chen, X. L. Ren, Y. C. Chen, et al., "Experimental Study on the Mechanism of High Hardness Circulating Water Fouling," *Industrial Water Treatment*, vol. 07, pp. 17-20, 2008.
- [5] H. S. Liu, "Study on the Treatment Technology of Circulating Cooling Water in Iron and Steel Enterprises," *Industrial Safety and Environmental Protection*, vol. 03, pp. 33-34+3, 2006.
- [6] J. Y. Xu, D. H. Xiong, S. X. Song, et al., "Superconducting Pulsating High Gradient Magnetic Separation for Fine Weakly Magnetic Ores: Cases of Kaolin and Chalcopyrite," *Results in Physics*, vol. 10, pp. 837-840, 2018.
- [7] C. T. Yavuz, A Prakash, J. T. Mayo, et al., "Magnetic Separations: From Steel Plants to Biotechnology," *Chemical Engineering Science*, vol. 64, no. 10, pp. 2510-2521, 2009.
- [8] D. W. Ha, T. H. Kim, M. H. Sohn, et al., "Purification of Wastewater From Paper Factory by Superconducting Magnetic Separation," *Transactions on Applied Superconductivity*, vol. 20, no. 3, pp. 933-936, 2010.
- [9] Y. Kakihara, T. Fukunishi, S. Takeda, et al., "Superconducting High Gradient Magnetic Separation for Purification of Wastewater from Paper Factory," *Transactions on Applied Superconductivity*, vol. 14, no. 2, pp. 1142-1145, 2006.
- [10] S. Q. Li, M. F. Wang, Z. A. Zhu, et al., "Application of Superconducting HGMS Technology on Turbid Wastewater Treatment from Converter," *Separation & Purification Technology*, vol. 84, no. 2, pp. 56-62, 2012.
- [11] H. Zeng, Y. Li, F. Xu, et al., "Feasibility of Turbidity Removal by High-gradient Superconducting Magnetic Separation," *Environmental Technology Letters*, vol. 36, no. 19, pp. 2495-2501, 2015.
- [12] N. S. Zaidi, J. Sohaili, K. Muda, et al., "Magnetic Field Application and Its Potential in Water and Wastewater Treatment Systems," *Separation and Purification Reviews*, vol. 43, pp. 206-240, 2013.
- [13] J. Liu and C. Li, "Experimental Study on Treatment of Heavy Metal Lead and Zinc Beneficiation Wastewater by Flocculant," *Applied Chemical Industry*, vol. 48, no. 05, pp. 1114-1118, 2019.
- [14] J. Sohaili, H. S. Shi, L. Baloo, et al., "Removal of scale deposition on pipe walls by using magnetic field treatment and the effects of magnetic strength," *Journal of Cleaner Production*, vol. 139, pp. 1393-1399, 2016.
- [15] K. W. Busch, S. Gopalakrishnan, M. A. Busch, et al., "Magnetohydrodynamic Aggregation of Cholesterol and Polystyrene Latex Suspensions," *Journal of Colloid and Interface Science*, vol. 183, no. 2, pp. 528-538, 1996.
- [16] V. Kozic and L. C. Lipus, "Magnetic Water Treatment for a Less Tenacious Scale," *Journal of Chemical Information and Computer Sciences*, vol. 43, no. 6, pp. 1815-1819, 2003.