UDC 504: 628. 162.1: 669.013.5: 681.8

Technology of Extraction Manganese Compounds from the Discharge Water of Metallurgical Enterprises with the Use of Ultrasound

L.A. Frolova, N.N. Shapa

Ukrainian State University of Chemical Technology

Research results of influence of ultrasound on the process of discharge water treatment from manganese compounds are considered. Possible chemical reactions describing a process are suggested. Influence of frequency and specific power of ultrasound on the process of discharge water treatment is established. A basic flow chart of the process is suggested.

Keywords: DISCHARGE WATER, MANGANESE COMPOUND, ULTRASOUND, TREATMENT CHART

Introduction

Recently the issues of industrial ecology are becoming more urgent in connection with substantial environmental degradation due to various emissions into the hydrosphere. The deterioration of water resources is associated with receipt of discharge water, often containing harmful substances in quantities exceeding the maximum allowable concentration. This problem is particularly relevant for the industrially developed regions. In Dnipropetrovsk region manganese ore is extracted and processed (and the main products of technological processes are ferrous alloys and steel alloys containing manganese). As a result, at metallurgical enterprises manganiferous discharge water is formed.

Currently, there are developed effective ways to clean discharge water from manganese cations. The most common are the sorption on ion exchange resins, setting, ozone oxidation and hydrodynamic cavitation [1, 2]. The latter method is of particular interest because it does not require the use of chemicals.

Results and Discussion

This paper suggests an alternative method of discharge water treatment by means of ultrasonic acoustic cavitation, i.e., irradiation of discharge water by a powerful stream of ultrasound. Unlike the hydrodynamic cavitation the process is more manageable and does not require the water supply with great speed.

Discharge water selected directly from the natural object was studied on the content of manganese by means of qualitative and quantitative analysis. The concentration of standardized test solutions of manganese salts were chosen similar to the values of manganese concentration in real discharge water to eliminate the influence of other impurities - iron cations, aluminum, cobalt, nickel, chromium, copper - on the test results and the course of the process.

Besides, the possibility of processing concentrated solutions of manganese salts, which can be formed in the etching rooms and other technical processes, such as mining-and-processing integrated works, during the production of ferroalloys, etc., was investigated in order to determine the possibility of their ulilization before entering the total mass of discharge water.

The main idea of the ultrasonic treatment is based on the effect of cavitation, which consists in the fact that upon passage of a powerful acoustic wave in a fluid there occur cavitation bubbles, in which pressure and temperature increase greatly, electrical discharges and explosions are produced, which can lead to various physical and chemical processes, not observed under other conditions [3].

A generalized mechanism involving the most probable processes that occur in the cavitation bubble can be written by the following chemical equations:

$H_2O + 1/2O_2 = H_2O_2$;

$3O_2 = 2O_3$;

$O_2 = 2O^-$;

$Mn^{2+} + 2O^- = MnO_2$.

In addition, hydrolysis of Mn^{2+} can occur in the solution, as well as the formation of permanganate ion, which in the neutral medium can interact with reducing agents and also become manganese dioxide.

The standardized test solution was subjected to ultrasound at an installation consisting of a ceramic reaction vessel in which an ultrasonic disperser radiator УЗДН–2Т is immersed connected to the generator of ultrasonic vibrations (**Figure 1**).

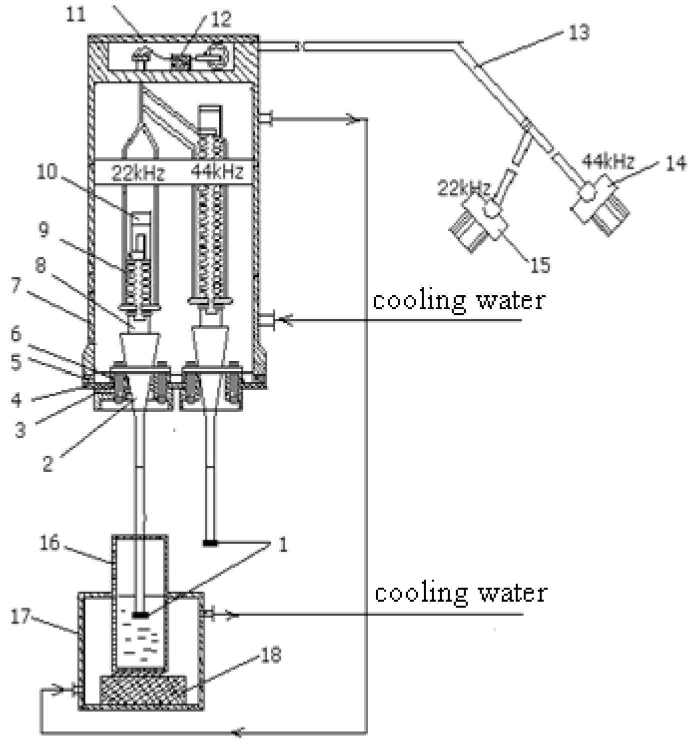

Figure 1. The laboratory setup: 1 - cone nozzle; 2 - concentrator 3, 5, 6, 10, 18 - rubber pads; 4 - bar; 7 - cover; 8 - magnetostrictive converter; 9 - coil; 11 - top cover; 12 - terminal lock; 13 - cable; 14, 15 - joints; 16 - ceramic glass; 17 - thermostating aluminum cover.

The influence of ultrasound was studied at two frequencies, 22 and 44 kHz and at various intensities of ultrasonic load ranging from 0.1 to 1 MW/m^2. Calculation of the ultrasound stress was carried out by dividing the power of the generator multiplied by the coefficient of energy use, and area of the radiator, which was calculated as the area of a circle. In the course of studies there were determined the concentration of manganese ions in the standardized test solution at different time intervals. After ultrasonic treatment the suspension was removed from the reaction vessel, the liquid was separated from the precipitation by filtration and analyzed for the presence of bivalent manganese ion in it.

The optimal treatment time was chosen in accordance with the previously composed plan of experiments.

Evident from these data (**Figures 2-4**) under the influence of ultrasonic treatment the content of manganese ions is reduced to a boundary concentration. This process depends on the intensity of ultrasound and is almost independent of its frequency. The optimum treatment time may be considered depending on the line parallel to the axis of time. Thus, when the generator power is about 1 MW/m^2, the maximum degree of purification is achieved within 10 min.

The studies on the ultrasonic treatment of concentrated solutions containing manganese, indicating the possibility of precipitation of manganese dioxide by ultrasound in aqueous solutions are also of great interest. At the same time a high degree of purification of manganese (97-98%) is achieved. The published data on the formation of permanganates under the influence of ultrasound were not confirmed within the study. This can be explained by the fact that in the investigated standardized test solutions the ion Mn^{2+} is hydrolyzed in the first stage, what facilitates the formation of precipitation, and released acid during the hydrolysis is not enough to shift the balance.

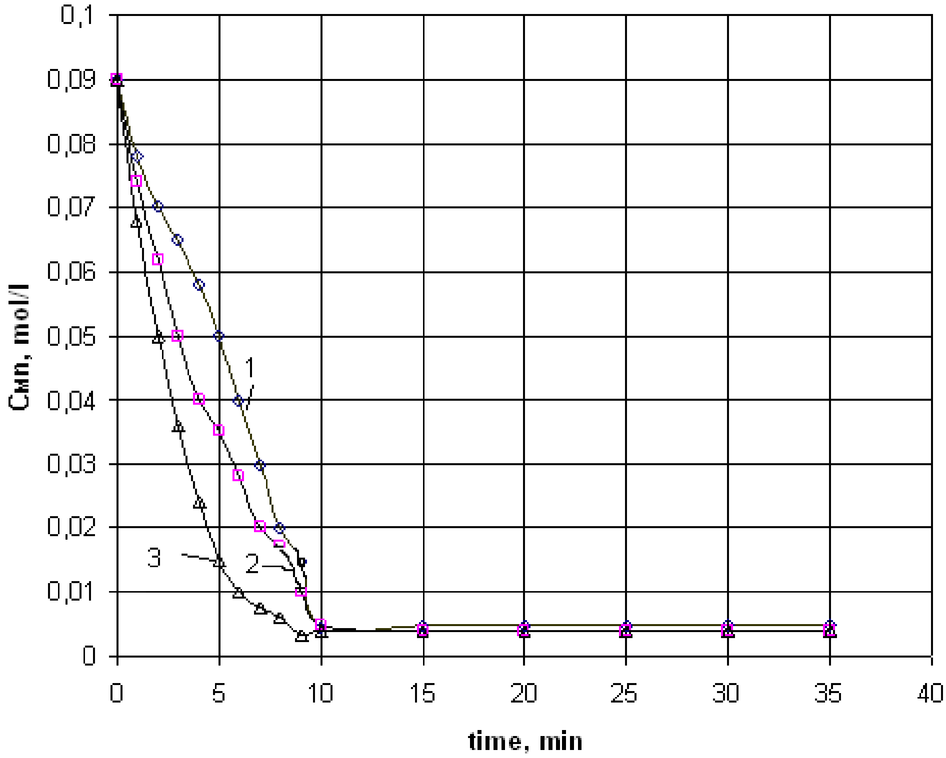

Figure 2. Dependence of concentration of Mn (II) in solution on the time of ultrasonic treatment at different power of the ultrasound flow (frequency 22 kHz), W/m^2: 1 – 10^5; 2 – $5 \cdot 10^5$; 3 – 10^6

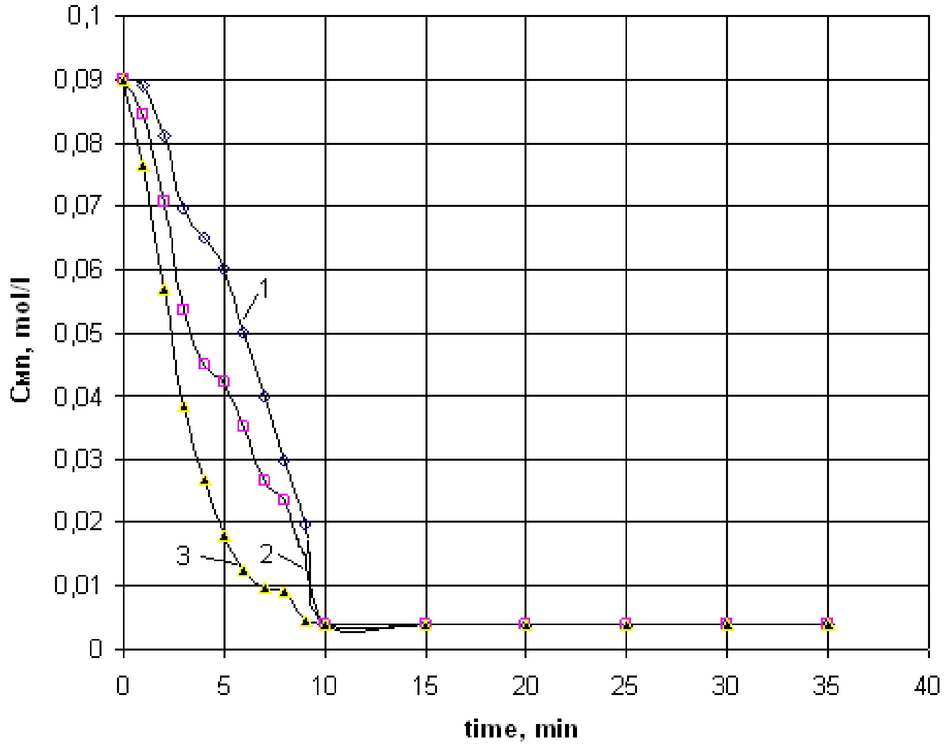

Figure 3. Dependence of concentration of Mn (II) in solution on the time of ultrasonic treatment at different power of the ultrasound flow (frequency 44 kHz), W/m^2: 1 – 10^5; 2 – $5 \cdot 10^5$; 3 – 10^6

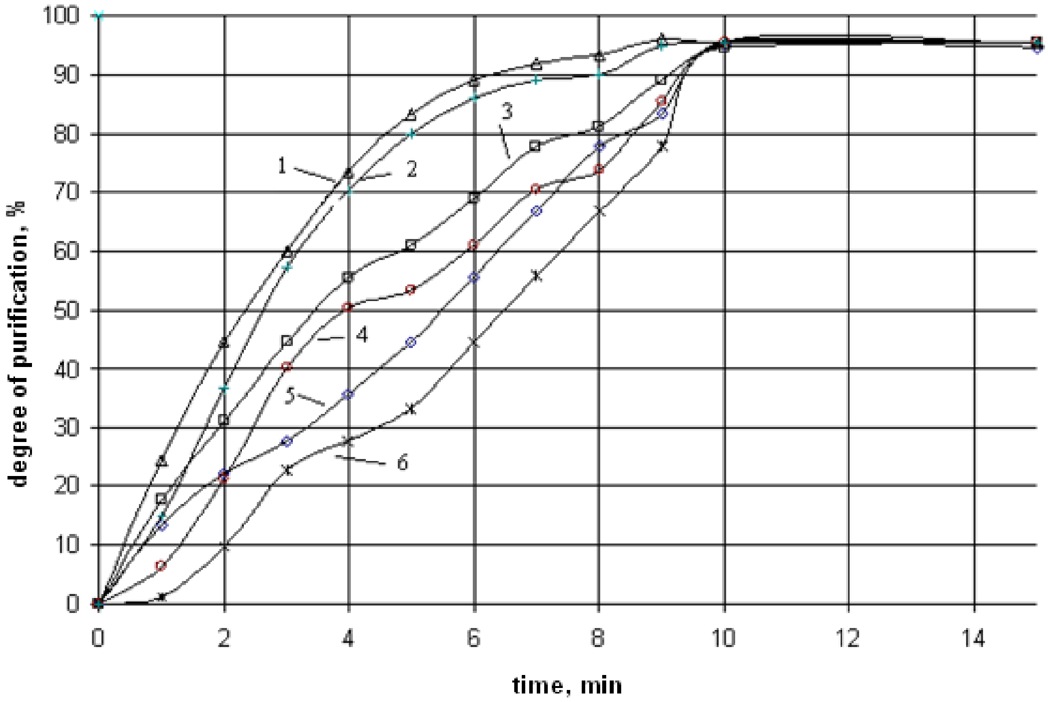

Figure 4. Dependence of the degree of wastewater purification from treatment time for different experimental conditions (frequency kHz, power W/m^2): 1 – frequency 22, power 10^6; 2 – frequency 44, power 10^6; 3 – frequency 22, power $5 \cdot 10^6$; 4 – frequency 44, power $5 \cdot 10^6$; 5 – frequency 22, power 10^5; 6 – frequency 44, power 10^5

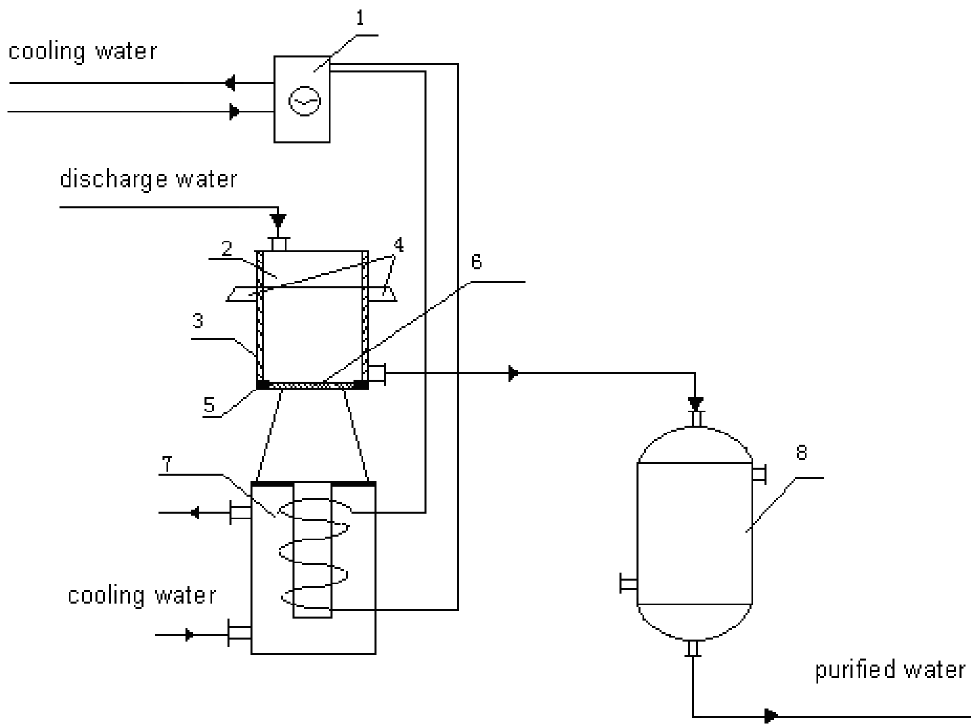

Figure 5. Schematic flow of sewage water from manganese compounds: 1 - high frequency generator; 2 - ultrasonic reactor; 3 - shell; 4 - supports; 5 - rubber lining; 6 - vibrating bottom; 7 - radiator block; 8 - granular filter

The studies confirm the applicability of the method of ultrasonic cavitation treatment for removing manganese ions. The data obtained during the described experiments were the source material for the development of the basic diagram and justification of the main parameters of the purification process of discharge manganese containing water.

The basic diagram of purification discharge water from manganese by ultrasonic treatment is shown in **Figure 5**.

The main unit is the ultrasonic reactor 2 where the discharge water is supplied and processed with ultrasound of low frequency with an intensity of about 10 MW/m^2 for within the optimum time (10 min). This unit can be made on the basis of semi-industrial ultrasonic equipment. A typical design of such a reactor is shown in **Figure 5** and consists of a generator of electrical oscillations of ultrasonic frequency 1, shell 3 suspended on supports 4, vibrating bottom 6 rigidly connected to the working part of the radiators block 7. Between the shell and vibrating bottom is a rubber lining 5. The oscillation generator and the radiator block are cooled by water to avoid overheating. After the reactor the treated discharge water is supplied in the filter 8 with granular charge for the sediment detachment, after which they are directed either for further purification and returned to the production cycle or dumped into the reservoir.

As the charge of granular filter it is recommended to use small coke or coal. It is advisable to use two filters, one of which works either in the loosening mode or is being repaired. It should be noted that the waste filter loading, which is sediment of manganese dioxide obtained by the discharge water treatment, and coke or coal, can be used in processes such as steelmaking, as components of the charge. In the case of discharge water utilization at a steel plant the waste filter charge can be utilized directly at this enterprise. This is one of the advantages of the suggested scheme.

Conclusions

The studies confirm the applicability of the method of ultrasonic cavitation processing for discharge water treatment in order to clean it from the ions Mn^{2+}. The data obtained in the described experiments can be used for development a specific technological scheme. The suggested scheme can be used for a batch or continuous process under the condition of providing the necessary for purification residence time of discharge water in the cavitation zone.

References

1. Ochistka stochnykh vod ot solyei margantsa, A.T. Dautova, K.F. Akhmadullina, S.V. Pestrikov, Mezhdunarodnaya molodezhnaya nauchn.-tekhn. konf. «Intellektualnye sistemy upravleniya i obrabotki informatsii», Ufa, 5-6 dekabrya, 2001: Tez. dokl., Ufa: Ufim. gos. aviats. tekhn. un-t, 2001, 305 p. *

2. Pat. 2183686 Rossiya MPK7 S 22 V 47/00, 3/24. Sposob izvlecheniya ionov margantsa iz vodnykh rastvorov, Voropanova Ya.A., Frolova N.V., № 2001101958/02; zayavl. 23.01.2001; opubl. 20.06.2002, Byul. № 17. *

3. Margulis M.A. Osnovy zvukokhimii. Khimicheskie ryeaktsii v akusticheskikh polyakh, M.: Vysshaya shkola, 1984, 273 p.*

* Published in Russian

Received August 8, 2011

Технология извлечения соединений марганца из сточных вод металлургических предприятий с использованием ультразвука

Фролова Л.А., Шапа Н.Н.

В статье представлены результаты исследований влияния ультразвука на процесс очистки сточных вод от соединений марганца. Предложены возможные химические реакции, описывающие процесс. Установлено влияние частоты и удельной мощности ультразвука на процесс очистки сточной воды. Предложена принципиальная технологическая схема процесса.