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REMOVAL OF MAGNESIUM IONS FROM WATER IN DIAPHRAGM ELECTROLYZERS

Bohdan VOSHCHENKO[1], Viacheslav RADOVENCHYK[1], Oleksii TOMIN[2]
[1]*Igor Sikorsky Kyiv Polytechnic Institute*
Beresteiskyi Ave, 37, Kyiv, 03056, Ukraine
[2]*Aalto University*
Otakaari 1, 02150 Espoo, Finland
e-mail: pbfpb21@gmail.com

Abstract

This work presents the results of a study on the applicability of electrolysis in two-chamber electrolyzers with a diaphragm for reducing magnesium hardness in aqueous solutions. It was established that conducting electrolysis for 10–60 minutes allows for a reduction in the initial water hardness from 10–30 mg-eq/dm³ to 7 mg-eq/dm³, which meets the current regulatory standards for potable water. The primary factor contributing to hardness reduction is the increase in pH in the cathodic compartment. A slight decrease in hardness was also observed in the anodic compartment, likely due to the diffusion of magnesium ions through the diaphragm into the cathodic chamber. When the electrolyzer is powered by a stabilized DC voltage source, a significant change in current density on the electrodes is observed during electrolysis, caused by the changing conductivity of the solution in the cathodic compartment. Under a constant chemical composition of water, this relationship may be used to monitor the progress of the electrolysis process. The promising results encourage further research in this direction.

Keywords: *electrolysis, water softening, magnesium hardness, magnesium ions (Mg^{2+}), magnesium hydroxide ($Mg(OH)_2$), diaphragm two-chamber electrolyzer, pH, precipitation, filtration, current density.*

The current state of natural water sources continues to deteriorate each year. In addition to anthropogenic pollution, climate change has a significant impact. As a result, the direct use of natural water is steadily decreasing, and most water sources require additional treatment [1]. This is especially true in industrial regions, where natural waters often require preliminary softening — the removal of calcium and magnesium ions.

Traditional softening methods, such as reagent and ion-exchange techniques, require complex equipment, high reagent consumption, and result in the generation of large volumes of waste. Therefore, researchers aim to develop more efficient water softening methods.

The potential of electrochemical methods for water softening has been known for a long time. A key feature of these technologies is the use of electrolyzers of various designs equipped with diaphragms or ion-exchange membranes [2] . However, despite the substantial number of scientific

publications, the practical application of this technology on an industrial scale remains limited. The main obstacle appears to be the high energy consumption required for large volumes of water and the low productivity of existing equipment.

In systems with low and medium productivity (such as domestic or office-scale units), lower electricity consumption and relatively small water volumes make it worthwhile to reconsider the use of electrochemical methods in this area. Therefore, the main objective of our study was to determine the feasibility and effectiveness of using electrolyzers of the appropriate design for water softening in low- and medium-capacity systems.

Electrochemical water softening involves the manipulation of the pH level in the compartments of a two-chamber electrolyzer equipped with a diaphragm. During electrolysis, a decrease in pH is observed in the anodic compartment, while a significant increase occurs in the cathodic compartment. Since electrolysis does not lead to the formation of compounds that can interact with hardness ions to produce insoluble precipitates, the main mechanism for hardness reduction lies in pH adjustment, i.e., the hydrolysis of these ions and their transformation into hydroxide forms [3].

Our experiments, based on pH regulation of the solution and separation of the resulting solid phase through filtration (Figure 1), demonstrated that magnesium ions undergo hydrolysis within a well-defined pH range. Specifically, at an initial magnesium hardness of 23 mg-eq/dm³, a reduction in residual hardness of the alkali-treated solution is observed only at pH ≥ 9.5, while a pronounced softening effect is recorded only at pH 11–11.5. Unfortunately, magnesium ions do not form low-solubility compounds with carbonate anions; therefore, under these conditions, carbonate has virtually no impact on their removal. Consequently, to effectively soften water with high magnesium hardness, it is necessary to maintain the pH in the cathodic compartment within the range of 11–11.5.

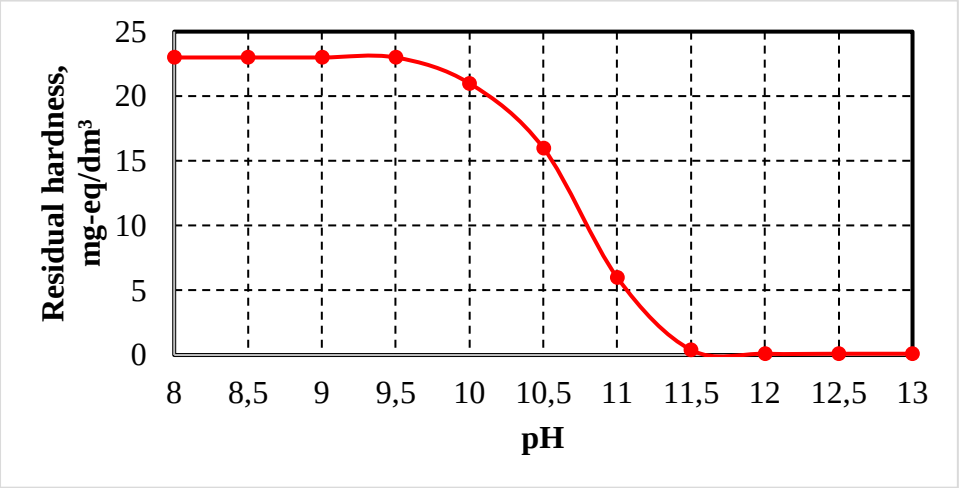


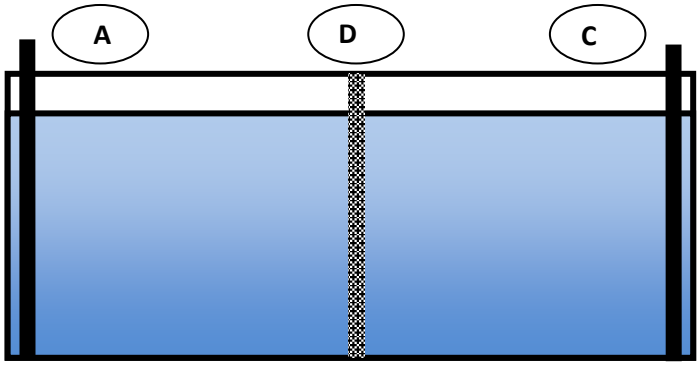
Fig. 1. *Degree of magnesium ion removal depending on pH level*

The efficiency of magnesium ion removal by the electrochemical method was studied using a two-chamber electrolyzer with a diaphragm made of "chlorinol" fabric, a lead anode, and a stainless-steel cathode, each with an area of 25 cm². The distance between the electrodes was 3 cm (Figure 2). Model solutions of varying concentrations were prepared based on $MgSO_4 \cdot 7H_2O$. The electrolyzer was powered by a stabilized DC voltage source ranging from 0 to 15 V.

The experiments demonstrated that, under appropriate conditions, results meeting the requirements of current regulatory standards can be achieved. For instance, at an initial magnesium hardness of 10.0 mg-eq/dm³, a sufficient pH level for the formation of magnesium hydroxide is reached in the cathodic compartment after 10–20 minutes of electrolysis (Figure 3). This pH level is maintained for

approximately 20 minutes before beginning to decrease due to the formation and precipitation of magnesium hydroxide. In the anodic compartment, pH stabilizes after about 10 minutes and remains relatively constant throughout the electrolysis process.

As the initial hardness of the solution increases, the time required to reach the target pH in the cathodic compartment also increases. At a hardness of 20.0 mg-eq/dm³, the necessary treatment duration is 30 minutes, while at 30.0 mg-eq/dm³, the required pH level is not achieved even after 60 minutes of electrolysis.



A – anode; C – cathode; D – diaphragm.

Fig. 2. *Two-chamber electrolyzer used for studying changes in solution parameters during electrolysis*

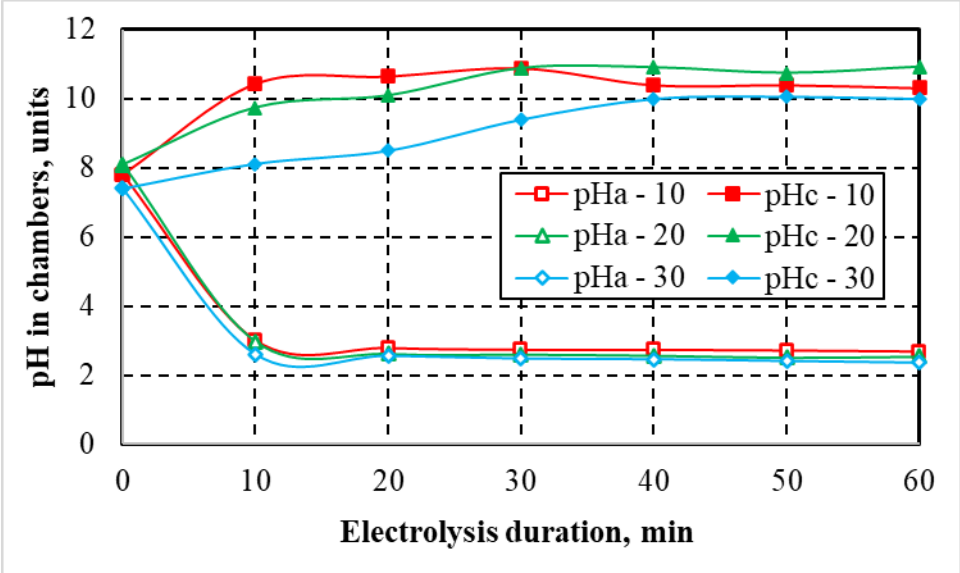


Fig. 3. *pH variation in the cathodic (pHc) and anodic (pHa) chambers over time during electrolysis at different initial Mg^{2+} concentrations: 10; 20; 30 mg-eq/dm³; U = 15 V*

A more critical parameter is the level of residual hardness after solution treatment. To assess it, the model solutions were filtered using "white ribbon" filter paper and analyzed for magnesium ion content. As shown in Figure 4, a decrease in hardness is recorded in both the cathodic and anodic compartments. It is evident that, during prolonged electrolysis, a portion of the magnesium ions diffuses through the diaphragm into the cathodic compartment, where they are converted into magnesium hydroxide. This is confirmed by the similar trend observed in the residual hardness curves in the anodic compartment over time.

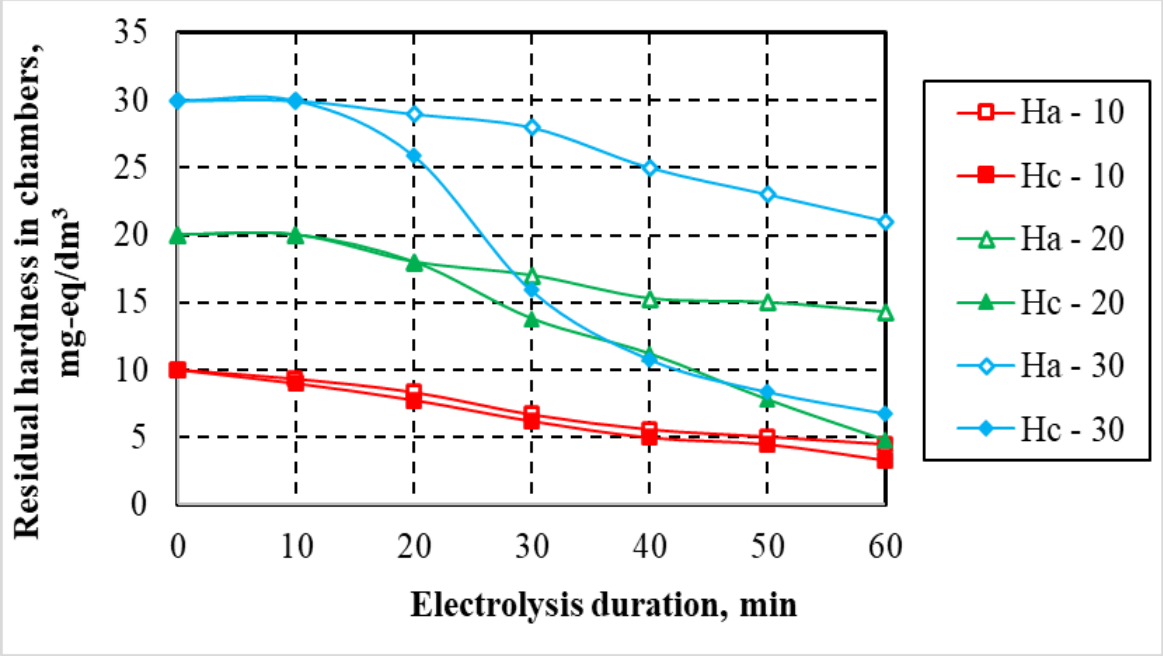


Fig. 4. *Residual hardness in the cathodic and anodic chambers over time during electrolysis at different initial Mg^{2+} concentrations: 10; 20; 30 mg-eq/dm³; U = 15 V*

At a low initial magnesium hardness (~10 mg-eq/dm³), the graphs showing hardness reduction over the course of electrolysis are nearly identical for both compartments, and the target hardness level of 7 mg-eq/dm³ is achieved within 25 minutes. Meanwhile, as shown in Figure 4, at higher initial hardness values, this standard level is barely reached even after 60 minutes, which is likely due to the tendency of magnesium hydroxide to form supersaturated solutions and the presence of a prolonged induction period [4].

Increasing the initial hardness of the solution to 20 mg-eq/dm³, and especially to 30 mg-eq/dm³, results in a significant change in the shape of the curves. The reduction in hardness in the anodic compartment increasingly lags behind that in the cathodic compartment. This suggests that, under identical electrolysis conditions, approximately the same amount of magnesium ions migrates through the diaphragm, leading to similar trends in residual hardness in the anodic compartment.

When a stabilized DC voltage of 15 V is applied to the electrodes, the hydrolysis of magnesium ions reduces the solution's conductivity, which in turn leads to a significant change in current density (Figure 5). It appears that under stable water composition, the extreme nature of this dependence could be used to monitor the electrolysis process. However, due to the unstable position of the extremum on the curves depending on the initial magnesium hardness, using this method to control the softening process in waters of varying composition is rather questionable.

Thus, the conducted studies demonstrated that electrolysis of water with a magnesium hardness level of 30 mg-eq/dm³ can yield satisfactory results if the treatment duration is up to 60 minutes. For lower initial hardness levels, this time can be reduced to 10–20 minutes. The initial concentration of magnesium ions determines the required electrolysis duration to achieve the regulatory standard of 7 mg-eq/dm³.

A reduction in water hardness is observed in both the cathodic and anodic compartments. In the latter, this effect is due to the diffusion of magnesium ions through the diaphragm into the cathodic chamber. During electrolysis, the concentration of magnesium in the cathodic compartment

decreases, leading to a corresponding reduction in current density on the electrodes.

Since the extreme change in current density significantly depends on the initial hardness of the water, using this parameter to control the electrolysis process appears questionable. The obtained results encourage further research focused on improving the design of electrolyzers, adjusting current density, and employing alternative electrode materials.

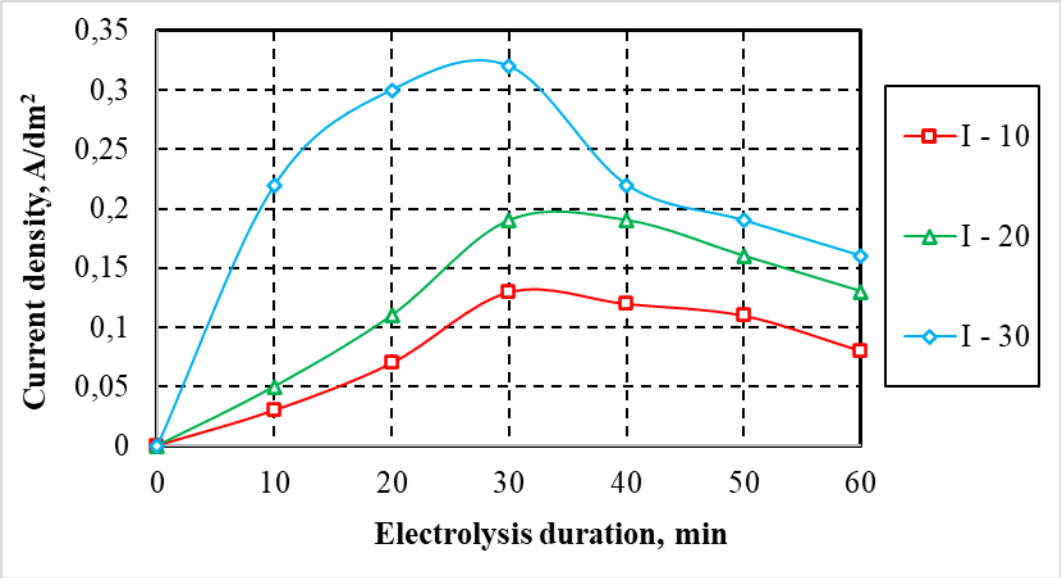


Fig. 5. *Change in current density during electrolysis at different initial Mg^{2+} concentrations: 10; 20; 30 mg-eq/dm³; U = 15 V*

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ВИДАЛЕННЯ ІОНІВ МАГНІЮ З ВОДИ В ЕЛЕКТРОЛІЗЕРАХ З ДІАФРАГМОЮ

Богдан ВОЩЕНКО
Київський політехнічний інститут імені Ігоря Сікорського
пр. Берестейський, 37, 03056, м. Київ,Україна
https://orcid.org/0009-0002-6502-0910

Вячеслав РАДОВЕНЧИК
Київський політехнічний інститут імені Ігоря Сікорського
пр. Берестейський, 37, 03056, м. Київ,Україна
https://orcid.org/0000-0001-5361-5808

Олексій ТОМІН
Університет Аалто
Otakaari 1, 02150 Espoo, Фінляндія
https://orcid.org/0000-0002-9927-6984

Анотація

У роботі наведено результати дослідження можливості застосування процесу електролізу в двокамерних електролізерах з діафрагмою для зниження магнієвої жорсткості водних розчинів. Встановлено, що проведення електролізу протягом 10–60 хв дозволяє знизити початкову жорсткість води з 10–30 мг-екв/дм³ до рівня 7 мг-екв/дм³, допустимого згідно з чинними нормативними документами для води, призначеної для споживання людиною. Основним чинником зниження жорсткості розчинів є зростання водневого показника в катодному відділенні. Деяке зниження жорсткості зафіксовано і в анодному відділенні, ймовірно, внаслідок дифузії іонів магнію через діафрагму в катодне відділення. При живленні електролізера від стабілізованого джерела постійної напруги зафіксовано екстремальну зміну щільності струму на електродах у процесі електролізу, спричинену зміною провідності розчину в катодному відділенні. За сталого хімічного складу води цю залежність можна використовувати для контролю перебігу процесу електролізу. Отримані позитивні результати стимулюють подальші дослідження в цьому напрямі.

Ключові слова: електроліз, пом'якшення води, магнієва жорсткість, іони магнію (Mg^{2+}), гідроксид магнію ($Mg(OH)_2$), двокамерний електролізер з діафрагмою, pH (водневий показник), осадження, фільтрація, щільність струму.