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Influence of Different Proportions of the Addition of Electrocoagulated Metal Sludge (EMS) Obtained from Oily Wastewater Treatment on the Properties of Laboratory Bricks

Morana Drušković ^{1,*} , Dražen Vouk ², Dajana Kučić Grgić ³  and Mario Šiljeg ⁴

¹ DOK-ING Ltd., Slavonska avenija 22 G, 10000 Zagreb, Croatia

² Water Research Department, Faculty of Civil Engineering, University of Zagreb, Fra Andrije Kacica-Miosica 26, 10000 Zagreb, Croatia; drazen.vouk@grad.unizg.hr

³ Department of Industrial Ecology, Faculty of Chemical Engineering and Technology, University of Zagreb, Trg Marka Marulića 19, 10000 Zagreb, Croatia; dkucic@fkit.unizg.hr

⁴ Josip Juraj Strossmayer Water Institute, Ulica Grada Vukovara 220, 10000 Zagreb, Croatia; siljeg.mario@gmail.com

* Correspondence: morana.druskovic@dok-ing.hr

Abstract: Electrochemical wastewater treatment technologies are increasingly being used in practice, and the combination of electrocoagulation with advanced oxidation processes has been shown to increase treatment efficiency. The treatment of oily wastewater produces electrocoagulated metal sludge (EMS). In this work, the possibility of using different ratios of EMS produced during oily wastewater treatment was investigated. EMS was dried conventionally in an oven at 105 °C and used as a partial substitute for clay in the manufacture of laboratory bricks. The main research objectives of this study were to examine the possibility and justification of introducing EMS in brick production. The results show that an increase in the proportion of EMS in the manufacturing of bricks leads to a deterioration in the quality of the bricks. Bricks with an addition of 1 wt% and 5 wt% EMS showed the best properties. The loss on ignition (LOI), compressive strength, boiling water absorption and initial water absorption were determined at 5.7%; 49 N/mm², 16%, 14 g/min/200 cm², 15% for modified bricks with 1 wt% EMS and 6.3%, 48 N/mm², 20%, 15 g/min/200 cm² for modified brick with 5 wt%.

Keywords: oily wastewater; EMS; bricks; compressive strength; water adsorption; LOI; ecotoxicity



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1. Introduction

In recent years, increasing amounts of waste have been generated worldwide. According to the European Union (EU), one citizen produces around 6000 kg of waste every year. A smaller proportion of the waste produced is recycled, while waste such as metal and plastic still ends up in landfill sites. The EU has issued regulations on waste management, such as the recovery and valorization of secondary raw materials [1,2].

Over the past few years, a growing focus has been directed to electrocoagulation (EC) processes in wastewater treatment. EC technology is being used more and more in real-life conditions to treat various types of wastewater. The EC process was first used at the end of the 19th century and its application to wastewater from various sources has been investigated. EC technology has demonstrated success in the treatment of wastewater contaminated with textile dyes, polymers and different organic substances, nitrates, phenols, arsenic, nutrients, drugs and bacteria, as well as in the treatment of landfill leachate, as well as potable water [3,4].

Electrocoagulated metal sludge (EMS) is produced during the treatment of wastewater by the electrocoagulation process, in which metal cations are released from the sacrificial anode in the reactor vessel under the influence of an electric field, which are required for

the coagulation/flocculation process with simultaneous oxidation of the water to O_2 and H^+ ions. At the cathode, water is reduced to ions (H^+ and OH^-), and O_2 is released at the anode. The most commonly used electrodes are made of iron (Fe^{2+}/Fe^{3+}) and aluminium (Al^{3+}) and the type of coagulate produced depends on them. Coagulants are insoluble metal hydroxide particles that remove the pollutants present in the wastewater through complex formation or electrostatic force. Coagulants are present in the shape of hydroxide ion monomers and highly charged polymeric metal hydroxide types such as $Fe(H_2O)_6^{3+}$, $Fe(H_2O)_5(OH)^{2+}$, $Fe(H_2O)_4(OH)^{2+}$, $Fe_2(H_2O)_8(OH)_2^{4+}$, $Fe_2(H_2O)_6(OH)_4^{4+}$, which neutralize the electrostatic charge on suspended solids and thus relieve agglomeration, which leads to separation from the aqueous phase through the deposition of EMS [5,6]. EMS contains organic and inorganic substances, bacteria, viruses, oils and fats, toxic heavy metals and trace metals as well as some nutrients such as nitrogen and phosphorus. It is chemically inert and does not release the pollutants that it removes from wastewater [7–13].

The EC process has been the subject of much research because it treats wastewater using electricity instead of chemical reagents, which are economically unacceptable and unfavourable and therefore require more complex handling. The EC process has proven successful in the removal of dissolved and colloidal contaminants in various industrial wastewaters, including food and textile industry wastewater treatment plants and other productions containing heavy metals, solutes, emulsifiers, organic substances and other pollutants [3].

The limit values of certain water quality parameters are prescribed by the Supervisory Authority (UPL) of each country for wastewater to be capable of release into the public sewerage system (PSS) and/or surface water bodies [14]. The treatment of wastewater always produces large quantities of treated wastewater and generated sludge, which must be disposed of properly. One of the possible techniques is to solidify the sludge and dispose of it in a landfill. The recycling and reuse of waste materials such as sewage sludge plays a crucial role in the preservation of the environment and the sustainable development of society. This sludge can be utilized as a building material in the production of bricks, concrete, roofing materials, tiles, building blocks, etc., if it fulfils all the necessary requirements [5].

In recent decades, the aim of waste policy has been to minimize the negative impacts of waste generation and management in order to mitigate the consequences for human health and the environment. Efforts must also be made to reduce the consumption of natural resources. The reutilization and recycling of waste materials should be a priority. The EU has introduced its own regulations on waste materials and the possibilities for their reuse [2]. Recently, there have been an increasing number of studies investigating the use of sludge from various sources as a substitute for part of the primary material in the construction of various building materials [15–17]. A relatively small number of studies have investigated the use of EMS as an alternative for part of the material for the manufacturing of construction materials. The use of EMS as a construction material is very useful because it transforms waste materials into valuable materials and reduces the amount that needs to be disposed of in landfills. One of the benefits of using sludge as an additive in construction materials is the oxidation of organic matter, the immobilization of potentially present toxic substances and heavy metals, and the destruction of pathogens during the annealing process [5].

Sharma and Josh [17] investigated the possibility of using sludge generated during the treatment of distillery spent wash by electrocoagulation, as a partial replacement for cement for the production of non-structural building blocks. The sludge was produced in a laboratory reactor with electrocoagulation. A stainless-steel electrode was used as the anode at a pH value of 7.8, a current density of 154.32 A/m^2 , a distance between the electrodes of 0.022 m and a reaction time of 135 min. The electrogenerated sludge was dehydrated in an oven at $110\text{ }^\circ\text{C}$ until it reached a uniform weight, then it was replaced in different percentages from 0–15% to reduce the amount of cement in the blocks. The results of the test showed that 7.5% is the ideal proportion of sludge that can be replaced by cement

with minimal change in physico-chemical properties. The building blocks produced in this way can be used in industry to make paving stones, pot making, garden fences, etc. without harming the environment.

Adyel et al. [5] investigated the use of electrocoagulated metal hydroxide sludge (EMHS), a by-product of wastewater treatment in the textile industry, as an integral component in the production of building blocks. The main characteristics of EMHS were Fe (87.1%), Mg (7.3%), Si (4.8%) and Ca (0.5%), while other elements were present in trace amounts (<0.1%). Two types of brick production were tested, normal (NBB) and pressurized (PBB) with different proportions of EMHS (10–50%) and firing temperatures (950 °C, 1000 °C, 1050 °C). The EMHS content and the firing temperature are the two most important factors that determine the quality of the bricks. A higher firing temperature and a higher proportion of EMHS in the mix lead to a higher weight loss and shrinkage of bricks. With a higher firing temperature and a lower ratio of EMHS in the mix, there was less water adsorption. The compressive strength increases with a higher firing temperature and a lower proportion of EMHS. NBB and PBB with the addition of 20 or 30% EMHS in the clay and a firing temperature of 1050 °C showed good properties and can be used for example decorative bricks, fences, etc. EMHS has the potential to be used as a component of building materials. This study has shown one of the possibilities for its use in the manufacture of bricks, but further research into its use is required. Some of the more interesting areas where EMHS can be used are concrete, ecological concrete, roads, plaster and mineral wool insulation [4].

In the tests by Hassan et al. [18], part of the clay was replaced by arsenic and iron containing sludge in varying proportions of 3%, 6%, 9% and 12%. The tests showed that the sludge content and the firing temperature are two decisive factors for the brick quality. The results of the compressive strength tests on brick samples indicated that the ratio of sludge strongly influences the strength of the bricks. The highest compressive strength value was achieved with an addition of 6% sludge, while a further increase in the sludge content led to a decrease in the value. It was found that the optimum quantity of sludge that can be mixed with clay to ensure a fine bond is 6%.

In this work, a study was carried out on the partial replacement of clay with EMS in the manufacture of bricks in order to obtain a quality product. The impacts of the addition of different proportions of sludge on the quality of the bricks produced, the initial adsorption of water, 5-h boiling water absorption, the compressive strength, the saturation coefficient, the ecotoxicity of the bricks, etc. were analyzed. The hypothesis of this study is that it is possible and justified to integrate EMS generated by the electrochemical process of oily wastewater into the production of bricks, which will lead to the production of innovative bricks with equivalent or improved properties. The aim of this study is to determine the optimal percentage for the utilization of EMS as a substitute of the clay in the manufacture of bricks.

2. Materials and Methods

2.1. Oily Wastewater of Mineral Origin

The oily wastewater was taken from a wet scrubber, i.e., from a flue gas cleaning system from the process of a higher stage thermal treatment of sewage sludge (gasification) produced in wastewater treatment plants (WWTP). Gasification produces waste gases that must be cleaned before they are released into the atmosphere. Wastewater from flue gas cleaning plants is referred to as oily wastewater of mineral origin, which must be treated in accordance with regulatory requirements before discharge to the environment or public sewer [13,19].

Multimeter (multiparameter) HI98194 pH/EC (electroconductivity)/DO (dissolved oxygen) (HANNA, Temse, Belgium) was used to measure certain water quality indicators, such as: water temperature, pH (resolution and accuracy: 0.001 pH, ± 0.002 pH), DO (resolution and accuracy: 0.01 mg/L, ± 0.2 mg/L), EC (resolution and accuracy: 0.05% FS and $\pm 1\%$ FS + 1 LSD) and TDS (total dissolved solids).

Spectrophotometer NANOCOLOR 500 D and heating block NANOCOLOR VARIO C2 (digestion time 2 h at 148 °C) manufactured by Macherey Nagel (Düren, Germany) was used to determine the chemical oxygen demand (COD) values (The reagents used are NANOCOLOR COD HR 1500 (for determination of COD in the range 20–1500 mg/L O₂) and NANOCOLOR COD 600 (for determination of COD in the range 50–600 mg/L O₂).

To determine the concentration of total hydrocarbons in wastewater samples was performed with an instrument from a Nexis GC-2030 system (Shimadzu, Kyoto, Japan). An extraction procedure was used to prepare the sample. This involved measuring 90 mL of wastewater sample (V_{sample}) and 5 mL of n-heptane extraction solvent in a beaker, which were then mixed with a magnetic stirrer for 30 min. After the separation of aqueous and organic phases in an extraction funnel, the organic phase, considered as the extract, was measured ($V_{extract}$) and 1 mL was transferred to a GC vial. Concentrations (c) of prepared samples were analyzed using GC. The concentration of total hydrocarbons ($c_{total\ hydrocarbons}$) is calculated using a specific formula:

$$c_{mineral\ oil} = \frac{c \times V_{extract}}{V_{sample}}$$

The GC is equipped with a split/splitless injector, an automatic liquid sampler and an FID detector. For optimal separation, an SH-Rxi-5MS column (30 m, 0.25 mm ID, 0.25 µm) was employed. The injector unit was set at 290 °C. The temperature program for the oven was initiated at 35 °C for 1.5 min, then increased to 60 °C at a rate of 5 °C/min, followed by a further increase to 315 °C at a rate of 5 °C/min, and maintained at this temperature for 10 min to precondition the column for subsequent analyses. Nitrogen served as the carrier gas at a constant flow rate of 1.77 mL/min. Each sample was injected in splitless mode with a volume of 1 µL. The detection limit (LOD) of the GC method is 0.01 mg/mL.

The analysis of the TOC (total organic carbon) in wastewater samples was carried out using ON-Line TOC-VCSH analyzer (Shimadzu, Kyoto, Japan). Before sample measurement, a calibration curve was developed by measuring the prepared amounts of potassium hydrogen phthalate. The sample was introduced to the syringe where it was sparged with synthesised air (N₂ and O₂ with flow of 150 mL/min) for 10 min (in case of NPOC measurements). Then, 50 µL of the solution was introduced to the Pt-catalyst in combustion tube which was heated at 680 °C. Afterwards, IR detector measured CO₂ from the sample.

2.2. EMS and Clay Samples

EMS is generated during the treatment of oily wastewater of mineral origin. Electrochemical processes were used to treat oily wastewater of mineral origin. The treatment of oily wastewater was carried out in three stages using stainless steel (SS), iron (Fe) and aluminium (Al) electrodes. The EMS was collected after the oily wastewater was treated using electrodes, settled and remained at the bottom of the container in which the treatment process was carried out. The EMS was then thermally treated and dried for 24 h at 105 °C in an MRC Mechanical Convection Oven DFO-240N (Holon, Israel). It was then crushed using a Gorenje BN1000W mixer (Velenje, Slovenia) and sieved through a U.S. sieve. Standard sieves of the ASTM Specification Fisher Scientific Company (Waltham, MA, USA) series with a size of 707 µm to reduce the particle size.

The clay used for this investigation was collected from the “Donja Čemernica” in Topusko, Croatia. The clay is prepared using the same process as EMS.

2.3. Characterization of Raw Materials

The content of oxides in EMS and clay was determined by atomic absorption spectroscopy using an AAnalyst 200 (PerkinElmer Inc., Waltham, MA, USA). The samples were initially dissolved by boiling in an acid mixture within steel autoclaves containing a Teflon cartridge, then diluted to the necessary volume and analyzed.

The EMS and clay samples were characterized by measuring the particle size. The particle size distribution was measured using a Malvern Mastersizer 2000 instrument

(Malvern, UK). The EMS and clay samples were first pulverized in a porcelain dish with light impact pressure, then dispersed in water (approx. 100 mg in 1 mL) and pre-treated with an ultrasonic probe (44 kHz, 190 W, steel tip, 3×20 s). The resulting dispersed sample (EMS, clay) was subsequently introduced into the flow cell of the device, and the particle size distribution was determined. A reference refractive index value of 1.65, characteristic of aluminium silicate, was used.

The moisture content of the EMS and clay samples was determined by drying at 105 °C until a stable weight was attained. An MRC DFO-240N dryer was used for drying.

Weight loss on ignition (LOI) was measured by calculating the before and after weight of the EMS and clay. An MRC Scientific Instruments Box Chamber Furnaces 1100 °C furnace was used for annealing.

The microstructure of the EMS and clay samples was determined using an electron microscope FE-SEM, Mira, Tescan (Brno, Czech Republic). The microscope can operate under low vacuum conditions, which prevents electrostatic charging of the sample surface. Technical features of the SEM device: resolution 1.0–3.0 nm, magnification $4 \times -1,000,000 \times$, electron gun: Schottky emitter with high brightness, scanning properties: dynamic focus, point and line scan, 3D light beam. EDS analysis of the samples was not performed in this study.

Before being analyzed, the samples (EMS, clay) were applied to the adhesive tape on the base. They then had to be steamed, as the samples were not conductive. The Q150T device from Quorum Technologies (Lewes, UK) was used to steam the samples. The samples are covered with a layer of metal ions (in our case it was chromium, Cr) to form a stable film, generating secondary electrons and thus providing a detailed image of the sample. Technical features of the vapour deposition device: vacuum of 1×10^{-6} mbar, current 0–150 mA up to the set film thickness or time, vapour deposition with chromium, 16 GB memory for storing more than 1000 user programmes.

The concentrations of the individual elements in the raw materials (EMS, clay) for brick production were analyzed using the energy-dispersive X-ray fluorescence technique (EDXRF). The radiation source is an X-ray tube with a molybdenum anode and a molybdenum secondary target, which are arranged at right angles to each other. The X-ray tube operated at 45 kV and 35 mA. The samples were irradiated for 1000 s in a vacuum and the spectra were collected using a Canberra Si(Li) detector with 3 mm thickness, 30 mm² active area, 0.025 mm Be window thickness, and a resolution of 170 eV (FWHM) at 5.9 keV. The spectra were analyzed using the IAEA QXAS 3.6 software and the concentrations of K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Ga, As, Br, Rb, Sr, Y, Zr, Pb, and Th were determined using the direct comparison of count rates with the IAEA-SL-1 (trace and minor elements in lake sediment) standard reference material.

2.4. Production and Characterization of Laboratory Bricks

EMS and clay were used to make the bricks prepared in the laboratory, the preparation of which is described in Section 2.1. After the materials (EMS, clay) were prepared for the production of bricks, the laboratory bricks were produced in the form of a disc (brick dimensions: diameter 50 mm, thickness 15 mm, weight 45–48 g). A total of 5 series of bricks were manufactured, namely control bricks made of 100% clay (without the addition of EMS) and bricks with the addition of EMS in various percentages of 1 wt%, 5 wt%, 10 wt% and 20 wt%. In brick production, it is also important to add the optimum amount of water to the raw materials for brick production. By adding water to the raw material mixture, the properties of the fired brick can be regulated, as the water replaces the air present in the mixture and, from a certain degree of saturation, occupies the space filled with raw particles. Therefore, the optimum amount of moisture plays a significant role in the production of bricks in order to achieve a higher degree of compaction of the EMS and clay [20,21]. Table 1 shows the proportions of clay and EMS used and the amount of water required for brick production.

Table 1. Mass proportion of raw materials in the mixture for brick production.

Raw Materials	Brick				
	Control	1% EMS	5% EMS	10% EMS	20% EMS
Clay	100	99	95	90	80
EMS	0	1	5	10	20
H ₂ O	31	33	30	30	37

For each series of laboratory bricks, 1800 g of material (EMS+clay) was used, which was mixed with a blender with the incorporation of water until a compact and homogeneous mixture was obtained that could be easily moulded. The prepared mixture was pressed into metal moulds. It was then left to stand in the moulds for several hours and then released from the mould by applying light pressure. The raw brick was then placed in a convection dryer MRC DFO-240N (Holon, Israel) at 105 °C for 24 h. After dehydrating, the brick was thermally treated in an annealing furnace (MRC Scientific Instruments Box Chamber Furnaces 1100 °C). Heating was carried out at a rate of 5 °C/min to 950 °C. The brick was then fired at this temperature for three hours and allowed to cool completely in the kiln (Figure 1). The surface of the sample must first be cleaned of materials left over from the production process. The dimensions of the diameter (d) and height (h) of the brick samples were determined using a sliding scale. For this test, it is necessary to use a tester that fulfils the measurement accuracy of 0.1 mm. After drying and firing, the size of the bricks was measured using a calliper prescribed by HRN EN 772-16:2011 [22] and weighed using a Kern ALT310-4AM analytical balance. LOI was measured by calculating the before and after weight of the bricks.



Figure 1. Production of modified laboratory bricks with different mass proportions of EMS (A) Sieved through sieve, (B) Homogenisation of solid raw materials, (C) Pressed into moulds, (D) Heat treatment in an annealing furnace and (E) Modified bricks.

The compressive strength of the prepared brick samples was determined using a FORM TEST press with a measuring range of 200 kN. Samples and tests were prepared with the HRN EN 772-1:2015 standard [23]. The sample was carefully levelled so that the maximum deviation did not exceed 0.1 mm per 100 mm. The surface of the test machine base was thoroughly cleaned and any remaining residue on the surface of the sample was removed. The sample was positioned exactly in the centre of the machine plate to distribute the load evenly. This test was performed on three samples for each batch of bricks produced and the result was averaged.

The initial water absorption tests were carried out according to the ASTM C67/C67M method [24], determination of water absorption of clay and calcium silicate masonry units by cold water absorption was determined according to the EN 772-21:2011 standard [25], while the water absorption of wall elements with moisture insulation layers was determined by boiling in water according to the EN 772-7:1998 standard [26]. Each of the tests was carried out on three tested samples for each set of bricks manufactured. The saturation coefficient, which represents the ratio between the cold water absorption by gradual immersion in water under normal atmospheric pressure over a period of 24 h and the water absorption by boiling in water for 5 h, was also determined.

The microstructure and element concentration of the individual elements of the modified bricks were analyzed using the same method described for EMS and clay samples in Section 2.1.

The ecotoxicity of a sample of modified bricks was determined using the bacterium *Vibrio fischeri*. The method for the determination of aerobic toxicity was carried out in accordance with the standard HRN EN ISO 11348-1:2000 Water quality–Determination of the inhibitory effect of water samples on the light emission of *Vibrio fischeri*, method using freshly prepared bacteria [27].

First, an eluate was prepared which consisted of the following steps. The brick samples were crushed and 5 g of a dry brick sample was weighed into an Erlenmeyer flask to which 50 mL of sterile deionized water was added and placed on a rotary shaker at 160 rpm. The sample was then homogenized for 24 h. The eluate was then filtered, and the filtrate was stored in the freezer until the ecotoxicity test. To analyze the ecotoxicity of the eluate on the marine bacterium *Vibrio fischeri*, the resuspension of the bacterium *Vibrio fischeri* and a 2% solution of sodium chloride (NaCl) were used. The LUMISTox 300 luminometer (Dr Lange GmbH, Hannover, Germany) was used to determine the acute toxicity of the eluate on the bioluminescent bacterium *Vibrio fischeri*.

3. Results and Discussion

3.1. Characterization of Oily Wastewater

The wastewater from the wet scrubber contains solid suspended particles and is characterized by an unpleasant odour and high organic load values. Table 2 shows the organic load values of the raw oily wastewater, the wastewater after electrochemical treatment and the legally prescribed limit values for discharge into surface water bodies, for the physical and chemical parameters such as pH value, dissolved oxygen (DO), electrical conductivity (EC), total dissolved solids (TDS), chemical oxygen demand (COD), total hydrocarbons, total organic carbon (TOC) and temperature (T).

Table 2. Physico-chemical parameters determined in raw water and treated oily water for each parameter and the upper permissible limit prescribed by Croatia (UPL_{CRO}) [19,28].

Parameter	Measurement Unit	Raw Water	Standard Deviation	After Treatment	UPL _{CRO}
pH	-	7.4–9.17	0.259	8.4	6.5–9.5
DO	mg/L	0.3–5.1	14.244	0.84	-
EC	mS/cm	1246–7330	1314.82	2995	2.5
TDS	mg/L	363–3637	692.31	1420	-
COD	mg/L	310–2000	610.02	152	700
Total Hydrocarbon	mg/L	3–143	47.38	1.16	30
TOC	mg/L	151–456	86.52	86.2	-
T	°C	22.8–28.1	0.821	31.5	40

3.2. Properties of Raw Materials

Table 3 Composition oxides (wt%) of the EMS and clay used for laboratory bricks expressed as mass percentage of each oxide in the sample (K₂O, MgO, Fe₂O₃, CaO, Na₂O, SiO₂, Al₂O₃ and TiO₂). The clay contains SiO₂, Al₂O₃, Fe₂O₃, CaO and MgO in concentrations of 66.52%, 14.59%, 5.49%, 0.72% and 0.63%, respectively, which is very similar to the standard clay. The main constituent of EMS is Al₂O₃ (20.06%), the content of which is slightly lower compared to standard clay samples. The high Al₂O₃ content could be due to the third stage of treatment of the oily wastewater, in which aluminium electrodes were used. A higher Fe₂O₃ content (13.15%) is also due to the use of iron electrodes, which were used in the second treatment stage. Rukijkanpanich and Thongchai [29] reported that high CaO content is favourable for the production of clay bricks as it helps to reduce porosity, which increases compressive strength. The SiO₂ content in EMS was 3.57%, far below that

of the standard clay sample. Other oxides, namely K_2O , MgO , Na_2O and TiO_2 , are also present in both EMS and clay samples, albeit in small amounts. During the firing process of clay bricks, these oxides help to increase the density and achieve better vitrification [18,30].

Table 3. Composition oxides (wt%) of the EMS and clay used for laboratory bricks.

Oxide Content	EMS (wt%)	Clay (wt%)	Standard Clay (wt%) [20,31]
K_2O	0.38	2.23	0
MgO	0.28	0.63	5
Fe_2O_3	13.15	5.49	8
CaO	1.37	0.72	1
Na_2O	1.21	1.49	-
SiO_2	3.57	66.52	55
Al_2O_3	20.06	14.59	30
TiO_2	0.03	1.36	-
Total	40.04	93.02	-

Particle size distribution and the optimization of the ratio of clay and non-clay materials play a key role in the manufacture of bricks with the desired properties, structures and characteristics [20,32,33]. In order to increase the plasticity and strength of the finished brick product, it is necessary to increase the proportion of clay minerals in the production process. Figure 2 shows the particle size distribution for the materials used in this study (EMS, clay). The graph shows that about 40% of the EMS particles are smaller than $2\ \mu m$ and belong to the clay fractions, about 20% of the particles are $2\text{--}20\ \mu m$ in size and belong to the dust fractions and about 35% of the present particles are larger than $20\ \mu m$ and belong to the sand fractions. In contrast, the clay used in this study contains a higher proportion of about 47% of particles smaller than $2\ \mu m$, which we refer to as clay fractions, and about 23% of particles within a size range of $2\text{--}20\ \mu m$, which belong to the dust fractions, while about 30% of the particles belong to the sand fractions larger than $20\ \mu m$. The finest particle size distribution in the clay could provide compactness in the fired bricks and in the wet state it also contributes to increasing the plasticity of the bricks [20,34–36].

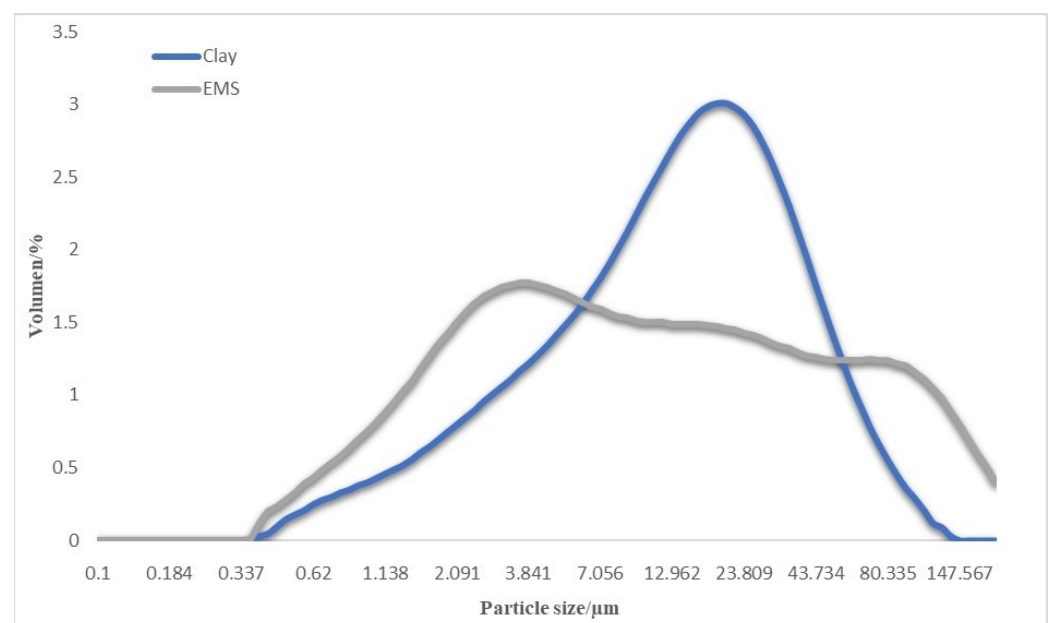


Figure 2. Particle size distribution of EMS and clay samples.

Adyel et al. [37] used sludge with similar properties to the EMS from this study in their monitoring. The sludge was replaced by part of the clay in the production of Normal

Building Blocks (NBBs) and Pressurised Building Block (PBB). According to their research, this sludge has a high specific gravity due to the high iron content and a high plasticity range if considered a soil-like material [38]. The extremely high liquid limit value of metal sludge might be due to the high moisture content of metal sludge. In this study, the moisture content of the decanted EMS sample was measured at 97.6% and that of the clay sample at 18%.

The high plasticity limit of the metal sludge is a consequence of the presence of organic substances that remain in the sludge after the treatment of oily wastewater with a high organic load (COD and total hydrocarbons). Most fine-grained soils exist naturally in the plastic state and the plasticity is due to the presence of clay minerals or organic minerals [39]. According to a study by Mitchell et al. [40], the more plastic the materials used to make bricks, the greater the shrinkage during drying. Herek et al. [34] found that the liquidity and plasticity of clay as well as its water content play an important role in determining the consistency of materials for the manufacture of brick products. Moist fine-grained clays exhibit plastic properties that depend on the moisture content bound in them.

At the beginning of the 20th century, Albert Atterberg defined the boundaries between different soil conditions. The determination of moisture values is referred to as Atterberg limits and includes the shrinkage limit (w_s), plastic limit (w_p) and liquid limit (w_L) [41,42]. According to the results of the Atterberg limits, the clay sample in the study has liquid and plasticity limits of 55% and 26%, respectively. The plasticity limit is 29%, the consistency index is 0.9 and the moisture content of the sample is 28% [43]. The mass loss during annealing depends on the amount of organic and inorganic constituents contained in the samples for brick production (EMS, clay). LOI during annealing was measured to be 71.49% for the EMS sample and 4.85% for the clay sample. These results show that the clay sample has optimum properties for brick production.

Figure 3 shows microscopic SEM images of conventionally dried EMS (A) and clay (B), taken at 2 μm magnification. The SEM images of the two samples show that they have a similar morphology. Glassy surface structures are visible on both samples, indicating the presence of SiO_2 in the composition of the sample [44]. The EMS sample (Figure 3A) has a porous surface, the particles have an irregular shape and a low dispersion. The particles of the electrochemical-generated sludge resemble magnetite, which is formed by oxidative hydrolysis of iron salts and is surrounded by smaller crystallites and spherical aggregates. The presence of spherical aggregates surrounding uniform crystals may be the result of the possible formation of other iron oxides such as maghemite or hematite [5,45]. SEM images of clay (Figure 3B) show polydisperse grains in a wide range of sizes and different shapes. Granular particles of irregular and platelet shape with a considerable degree of agglomeration predominate. This structure corresponds to the morphology of kaolin [34,46].

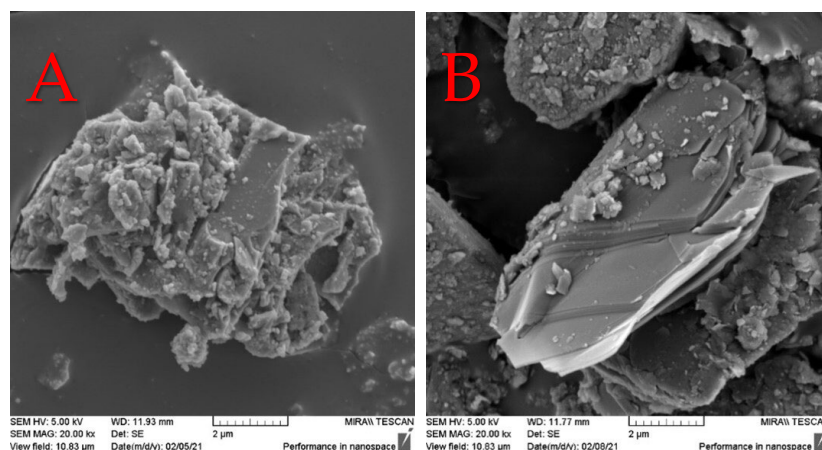


Figure 3. SEM images of EMS (A) and clay (B) at 2 μm .

The content of the individual elements in the EMS and clay samples is listed in Table 4. The amount of each element in the EMS and clay samples was determined using the energy-dispersive X-ray fluorescence (EDXRF) measurement technique. From the table, we can see that EMS and clay contain inorganic components in their composition. The inorganic component in the EMS indicates that the wastewater contains concentrations of certain elements in its composition, which were precipitated together with the sludge produced during the treatment process. The increased concentrations of Fe and Ca in the EMS and clay samples show that these materials contain oxides in their composition. Larger amounts of Fe, Mn, Cr, Zn, Ni and Cu in the EMS sample are the result of the use of electrodes made of SS, Fe and Al, which contain the mentioned elements in their composition, which is why this sludge must not be dumped on the ground [34]. Due to the metal content and the physical and chemical composition of the EMS and clay samples, it is assumed that they are suitable for brick production.

Table 4. Mass concentrations and their standard deviations (SD) of elements in EMS and clay.

Element	Mean $\pm$ STD	EMS	Clay
K	ppm	$1.8 \times 103 \pm 0.03$	$1.96 \times 104 \pm 0.29$
Ca	ppm	$1.62 \times 104 \pm 0.09$	$2.5 \times 103 \pm 0.01$
Ti	ppm	$1.75 \times 102 \pm 24.49$	$6.72 \times 103 \pm 562.29$
V	ppm	$1.01 \times 101 \pm 1.84$	$1.77 \times 102 \pm 16.55$
Cr	ppm	$2.79 \times 102 \pm 26.77$	$9.05 \times 101 \pm 9.93$
Mn	ppm	$1.31 \times 103 \pm 61.32$	$3.13 \times 102 \pm 15.15$
Fe	ppm	$7.73 \times 107 \pm 0.2$	$4.15 \times 107 \pm 0.11$
Ni	ppm	$1.48 \times 102 \pm 28.62$	48.9 ± 9.47
Cu	ppm	$8.5 \times 101 \pm 17.07$	$5.5 \times 101 \pm 11.17$
Zn	ppm	$4.41 \times 102 \pm 441.3$	$1.12 \times 102 \pm 5.23$
Ga	ppm	$3.33 \times 101 \pm 7.23$	$2.28 \times 101 \pm 4.97$
As	ppm	6.4 ± 0.69	$1.68 \times 101 \pm 1.78$
Br	ppm	4 ± 0.27	<0.5
Rb	ppm	8.3 ± 0.82	$1.44 \times 102 \pm 14.06$
Sr	ppm	$1.04 \times 102 \pm 55.76$	$9.7 \times 101 \pm 52.3$
Y	ppm	4.3 ± 0.31	$1.07 \times 102 \pm 5.41$
Zr	ppm	$6.3 \times 101 \pm 3.68$	$6.32 \times 102 \pm 32.4$
Pb	ppm	9.3 ± 1.9	$3.16 \times 101 \pm 6.26$
Th	ppm	<0.89	$1.74 \times 101 \pm 1.363$

3.3. Quality of Bricks

The prepared laboratory bricks were first analyzed to determine whether the shape and size of the bricks changed during the drying and firing process or whether the bricks cracked [47]. All bricks had the desired shape and size and there were no deformations that can occur when firing bricks at high temperatures. The length, height and width of the brick samples were measured according to HRN EN 772-16:2011. According to studies by Aldey et al. [5], the most important criteria for evaluating the quality of bricks are compressive strength, weight loss during annealing, shrinkage during annealing and water adsorption.

The LOI of bricks during firing depends on the amount of organic and inorganic materials present in EMS and clay [20]. The percentage weight loss during annealing as a function of EMS content is shown in Figure 4. An increase in the EMS content in the bricks leads to an increase in weight loss when the bricks are annealed. The lowest weight loss during annealing of 5.71% was observed in bricks with 1% EMS. The organic content of EMS and clay was 28.51% and 3.6%, respectively. Since the weight loss is highly dependent on the organic content, the percentage of weight loss increases with the increase in the proportion of EMS in the modified bricks. The ASTM C62-17 standard [48] was used to determine the weight loss.

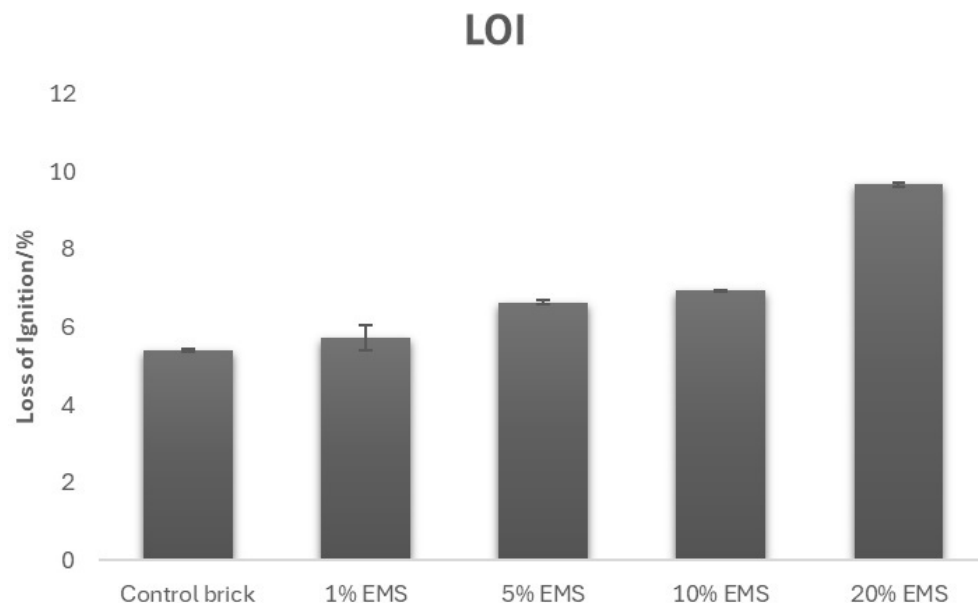


Figure 4. Mean value percentage of weight loss of EMS-incorporated fired bricks.

Dai et al. [49] have shown in their investigations that all organic materials burn completely below 950 °C when bricks are fired. The carbonates present in the clay and sludge are broken down and released as CO₂. This phenomenon was also observed in several other brick manufacturing studies with tannery sludge [50,51], sewage sludge [52] and paper mill sludge [53], which showed a weight loss of 16.5%, 14% and 18.84%, respectively. In this study, the highest weight loss was 10.12%, which is within the criteria prescribed by the ASTM C62-17 standard ($\leq 15\%$) [52].

The most important mechanical property that a brick must fulfil in order to be used as a building element is its compressive strength. This property indicates the ability of the material to resist forces until it breaks. In this study, the compressive strength depends on the amount of EMS that is replaced by clay. The higher the compressive strength values of the tested material, the material's overall porosity decreases. In addition, bricks with higher compressive strength values have a lower resistance to damage caused by freezing and thawing cycles [5,35,54,55].

The results of the study show that the compressive strength strongly depends on the amount of EMS added to the bricks, as shown in Figure 5. Higher EMS content in the bricks results in decreased compressive strength. The compressive strength value for the control brick was determined to be 50 N/mm². Bricks with the addition of 1 wt% and 5 wt% EMS exhibited approximately the same compressive strengths, namely 49 N/mm² and 48 N/mm². When the EMS content was increased to 10% by weight, the compressive strength was 32 N/mm². When the weight percentage of EMS was increased to 20%, the compressive strength decreased further to 17 N/mm². We can relate these results to the results of the amount of water adsorbed by boiling for 5-h (Figure 6). The amount of water adsorbed during the 5-h boil is inversely proportional to the compressive strength. This means that as the compressive strength of the brick decreases, the water absorption of the brick increases during the 5-h boil.

Figure 6 shows the water adsorption during a 5-h boiling process in bricks with 1 wt%, 5 wt%, 10 wt% and 20 wt% EMS. The parameter for water adsorption during the 5-h boil showed a linear increase the higher the EMS content in the bricks. According to the standard regulations, the values for absorption during the 5-h boil should be 17–20% [56]. According to the mentioned regulations, the bricks with 1 wt% and 5 wt% EMS addition, i.e., 16% and 20%, met the prescribed conditions.

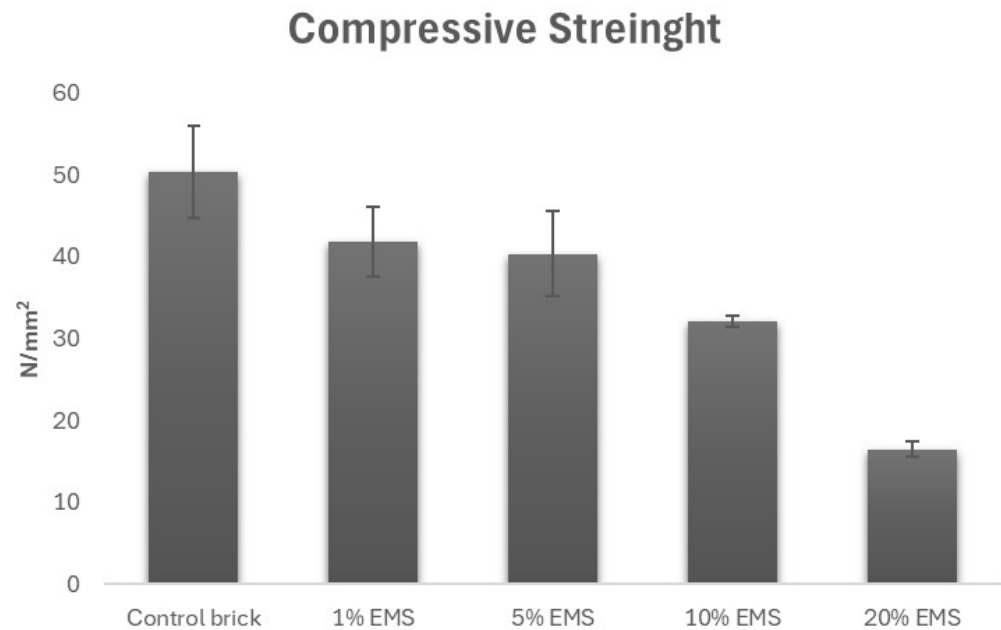


Figure 5. Mean value compressive strength of EMS incorporated fired bricks.

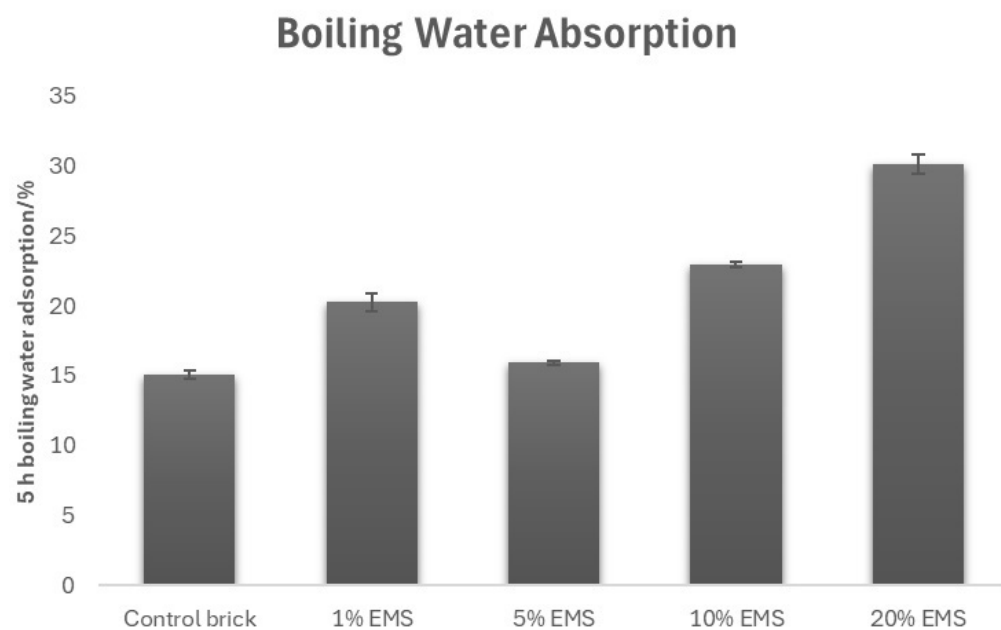


Figure 6. Mean value boiling water absorption of EMS incorporated fired brick.

The amount of initial water absorption depends on the number, size and shape of the micropores in the brick structure. Figure 7 shows the initial water absorption for the control bricks and the bricks with the addition of 1 wt%, 5 wt%, 10 wt% and 20 wt% EMS. The graph shows that the initial water absorption increases with increasing EMS content in the bricks [44,57,58].

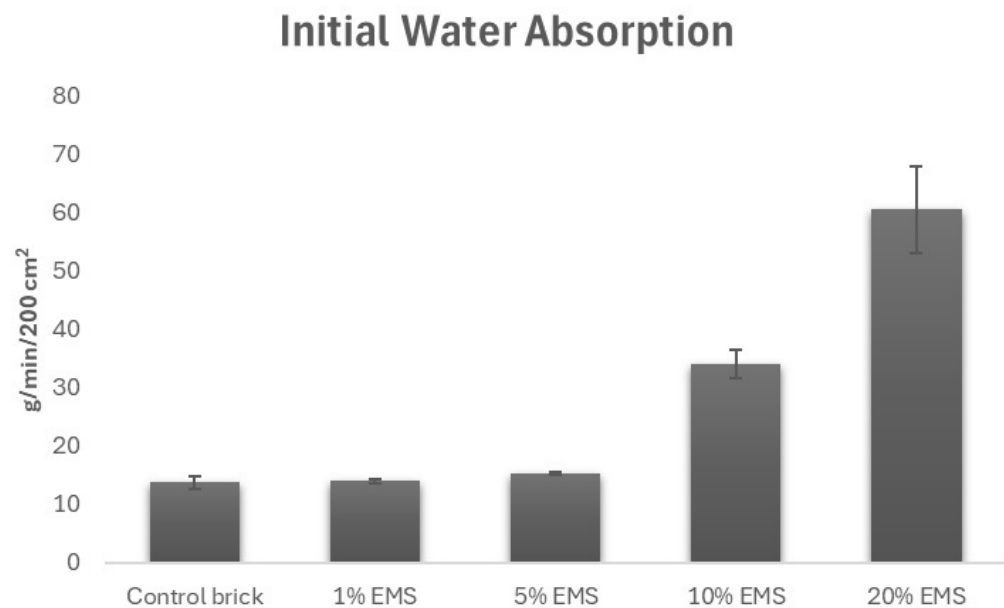


Figure 7. Mean value initial water absorption of EMS incorporated fired brick.

The water absorption values are shown in Figure 8 for the control bricks and the bricks with the addition of 1 wt%, 5 wt%, 10 wt% and 20 wt% EMS. Raimondo et al. [57] have shown a linear correlation between water absorption and open porosity. Water absorption is a significant parameter that indicates brick durability. Lower values correspond to greater resistance of the brick to external influences. In the study by Kadir et al. [59], the water absorption of normally fired bricks should be 5–20%. The water absorption values for bricks incorporating 1 wt% (15%), 5 wt% (15%), 10 wt% (17%) and 20 wt% (20%) EMS all met the specified requirements.

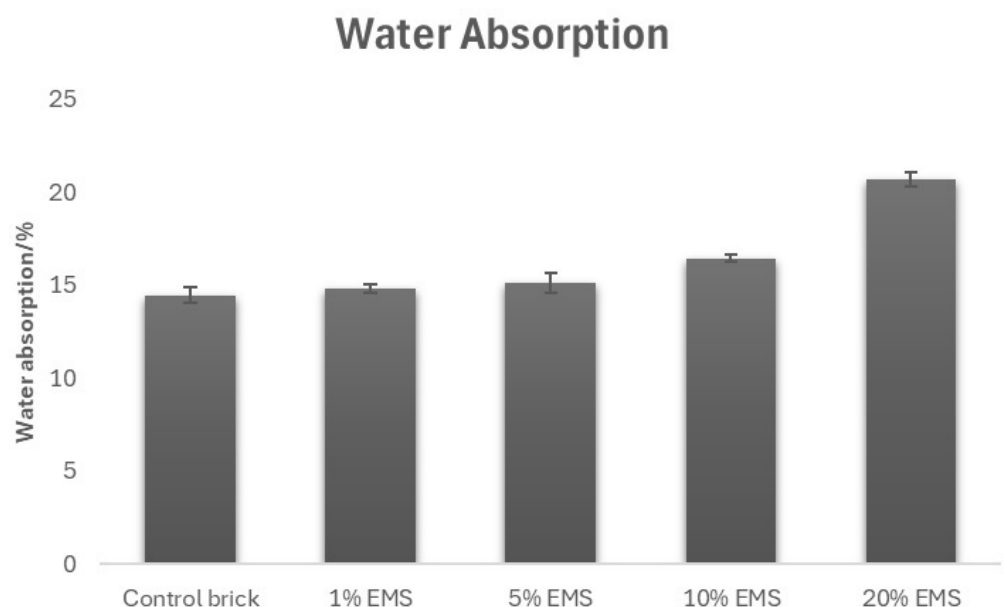


Figure 8. Mean value water absorption of EMS incorporated fired brick.

The saturation coefficient determines the ratio between the pores that can be easily filled with water and the total pore volume. This parameter reflects the durability of the material, i.e., the free space in the pore volume that remains after they have been filled with water. It is also proportional to the proportion of medium-radius pores and can be related to the pore size. In a structure with a large number of large pores, the saturation coefficient

increases, while it decreases with a larger number of fine pores. According to Canadian and American standards, the maximum permissible saturation coefficient, the so-called “critical” saturation coefficient, which ensures resistance to freeze–thaw cycles, depends on the raw material used for production and the method of brick production and is between 0.75 and 0.8 [56,60–62].

The values of the saturation coefficient of the modified bricks were slightly lower than those prescribed by the standards. The saturation coefficient for the brick sample with the addition of 20 wt% EMS was lower (0.69), which is probably due to the manual production of the bricks, while the values for the bricks with 1 wt%, 5 wt% and 10 wt% were 0.91, 0.75 and 0.72, respectively (Figure 9).

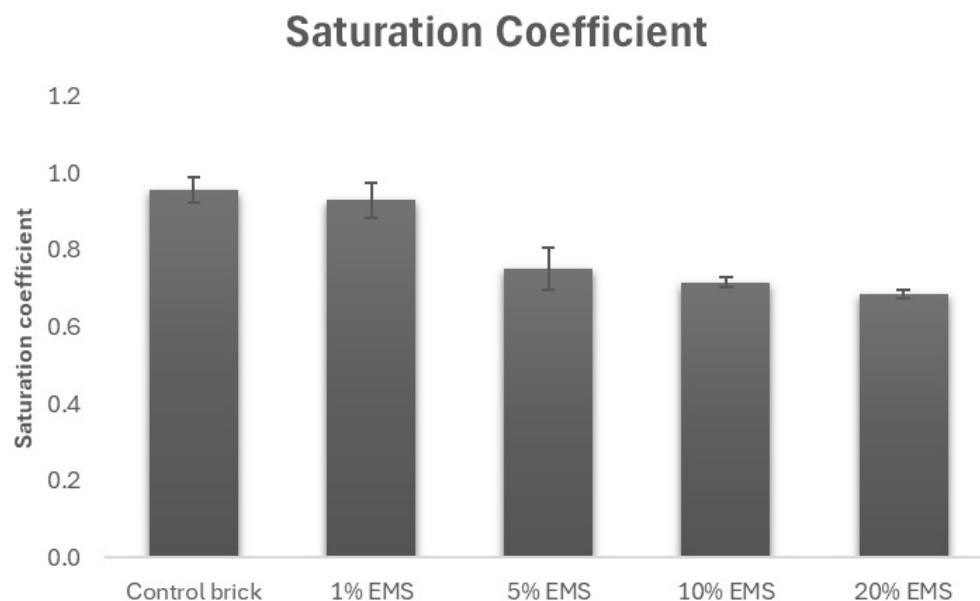


Figure 9. Mean value saturation coefficient of EMS incorporated fired brick.

The following figures show SEM images of the brick remains obtained after breaking, namely Figure 10, which shows a control brick made of 100% clay, and Figure 11, which shows a brick with 1% EMS, 5% EMS, 10% EMS and 20% EMS. The images show that the broken bricks have a layered microstructure. Bricks with 1%, 5%, 10% and 20% replacement of EMS by clay show larger glassy phases compared to the reference brick made of 100% clay. Glassy phases have isolated pores with a size of about 5–15 μm [63].

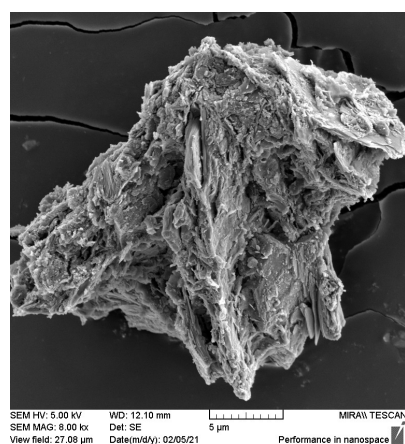


Figure 10. SEM images of the fired control brick.

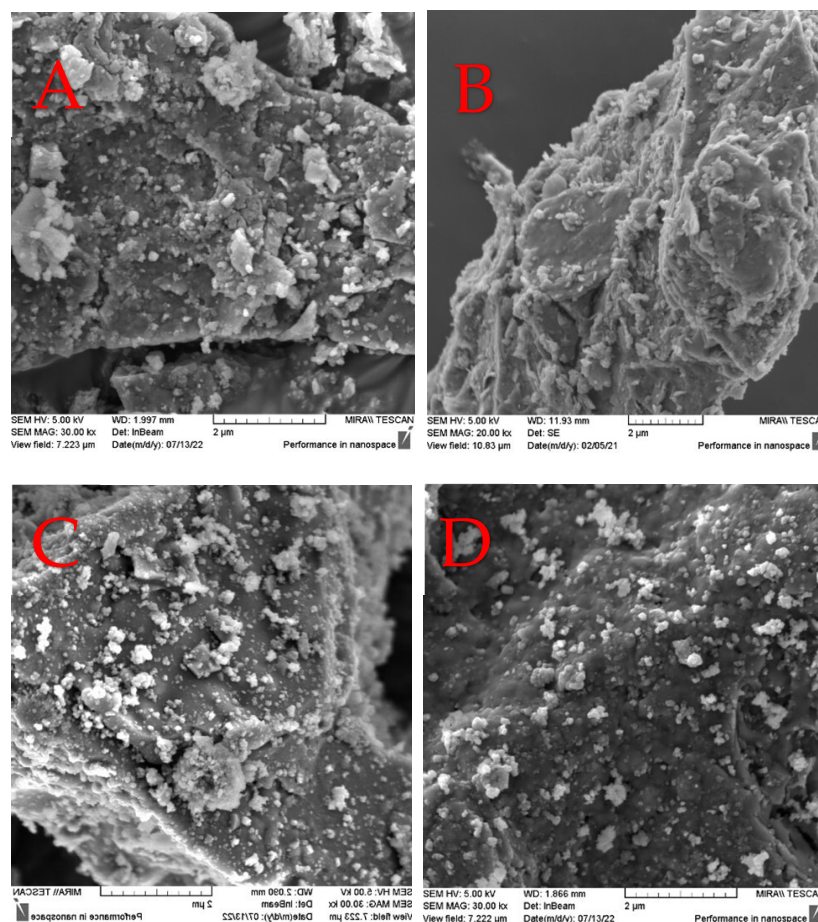


Figure 11. SEM images of the fired brick (A) 1% EMS, (B) 5% EMS, (C) 10% EMS and (D) 20% EMS incorporated brick.

Cheeseman et al. [64] investigated the sintering of 100% sewage sludge ash (SSA). At 1040 °C it forms a relatively low-density material that appears hard and well sintered with a glassy surface. SEM images of broken brick surfaces showed that they contain a considerable volume of isolated, spherical pores with a size of 20–30 μm. A similar phenomenon occurred in the investigations of Ottosen et al. [65], where the appearance of spherical pores was due to bloating. The conditions that must be met for this phenomenon to occur are: The material needs to reach a glassy high-temperature phase with sufficient viscosity to keep the gas, and the substance present in the material must release the gas at the temperature at which the glassy phase forms. Riley [66] found in his research that pyrite, hematite and dolomite have the necessary constituents to release gas at a high enough temperature to cause bloating. EMS contains hematite in its composition, which was probably involved in the bloating of the sintered phases.

In their study, Herek et al. [34] used textile laundry sludge produced as a substitute for some of the clay used in the manufacture of bricks. SEM images of ceramic bricks with different sludge contents of 5%, 12%, 16%, 20% and 24% showed a rough and porous structure. This structure is characteristic of clay bricks. In general, an increase in the sludge content in bricks leads to an increase in surface smoothness [67].

Metals contained in EMS solidify when they are added to bricks. The mechanisms of solidification of slurries containing metals can be physical encapsulation, adsorption and precipitation. In physical encapsulation, EMS encapsulates the contaminated particles due to the content of small pores. The absorption of EMS, which contains a large number of micropores resulting in a large specific surface area, leads to easy adsorption of metal ions on crystallized particles. By precipitation, hydration products of the cement such as Ca(OH)_2 create a strongly alkaline environment, which leads to easy conversion of the

metals into hydroxides, which have a very low solubility. The content of the individual elements in the control brick and in the modified bricks is shown in Table 5.

Table 5. Content of element in control, 1% EMS, 5% EMS, 10% EMS and 20% EMS incorporated brick.

Element	Mean $\pm$ STD	Control	1% EMS	5% EMS	10% EMS	20% EMS
K	ppm	$1.95 \times 104 \pm 0.28$	$1.81 \times 104 \pm 0.26$	$1.72 \times 104 \pm 0.25$	$1.65 \times 104 \pm 0.24$	$1.39 \times 104 \pm 0.20$
Ca	ppm	$0.28 \times 104 \pm 0.02$	$2.58 \times 103 \pm 147$	$0.29 \times 104 \pm 0.02$	$2.75 \times 103 \pm 156$	$3.59 \times 103 \pm 206$
Ti	ppm	$6.31 \times 103 \pm 528$	$6.21 \times 103 \pm 520$	$6.02 \times 103 \pm 504$	$5.56 \times 103 \pm 466$	$5.19 \times 103 \pm 436$
V	ppm	$1.69 \times 102 \pm 16.0$	$1.47 \times 102 \pm 14$	$1.55 \times 102 \pm 14.4$	$1.4 \times 102 \pm 13$	$1.52 \times 102 \pm 14$
Cr	ppm	$1.26 \times 102 \pm 13.4$	$1.85 \times 102 \pm 18$	$1.16 \times 102 \pm 11.7$	$6.54 \times 102 \pm 64$	$1.39 \times 103 \pm 135$
Mn	ppm	$4.36 \times 102 \pm 21$	$3.76 \times 102 \pm 18$	$4.80 \times 102 \pm 23$	$6.61 \times 102 \pm 32$	$1.10 \times 103 \pm 53$
Fe	ppm	$4.38 \times 104 \pm 0.11$	$4.52 \times 104 \pm 0.11$	$4.98 \times 104 \pm 0.13$	6.66 ± 0.17	9.72 ± 0.25
Ni	ppm	$4.66 \times 101 \pm 9.0$	$4.73 \times 101 \pm 9.1$	$6.49 \times 101 \pm 12.5$	$1.46 \times 102 \pm 27.8$	$2.09 \times 102 \pm 39.9$
Cu	ppm	$4.0 \times 101 \pm 8$	$2.95 \times 101 \pm 5.9$	$3.3 \times 101 \pm 7$	$3.64 \times 101 \pm 7.3$	$3.7 \times 101 \pm 7.5$
Zn	ppm	$1.02 \times 102 \pm 4.8$	$8.83 \times 101 \pm 4.1$	$1.06 \times 102 \pm 4.9$	$1.52 \times 102 \pm 6.9$	$2.14 \times 102 \pm 9.8$
Ga	ppm	$2.14 \times 101 \pm 4.7$	$2.17 \times 101 \pm 4.7$	$1.94 \times 101 \pm 4.2$	$2.23 \times 101 \pm 4.8$	$1.18 \times 101 \pm 4.0$
As	ppm	$2.23 \times 101 \pm 2.4$	$1.78 \times 101 \pm 1.9$	$1.84 \times 101 \pm 2.0$	$1.62 \times 101 \pm 1.7$	$1.20 \times 101 \pm 1.3$
Rb	ppm	$1.41 \times 102 \pm 13.7$	$1.33 \times 102 \pm 13.0$	$1.28 \times 102 \pm 12.4$	$1.11 \times 102 \pm 10.8$	$8.65 \times 101 \pm 8.4$
Sr	ppm	$9.2 \times 101 \pm 49$	$8.6 \times 101 \pm 46$	$8.2 \times 101 \pm 44$	$7.4 \times 101 \pm 40$	$6.0 \times 101 \pm 32$
Y	ppm	$9.72 \times 101 \pm 4.9$	$8.78 \times 101 \pm 4.4$	$9.08 \times 101 \pm 4.6$	$8.09 \times 101 \pm 4.1$	$6.43 \times 101 \pm 3.2$
Zr	ppm	$5.25 \times 102 \pm 27$	$4 \times 102 \pm 20$	$4.87 \times 102 \pm 25$	$3.42 \times 102 \pm 17$	$3.05 \times 102 \pm 16$
Pb	ppm	$3.92 \times 101 \pm 7.8$	$3.06 \times 101 \pm 6.0$	$3.01 \times 101 \pm 6.0$	$3.27 \times 101 \pm 6.5$	$2.24 \times 101 \pm 4.4$
Th	ppm	$1.49 \times 101 \pm 1.23$	$1.81 \times 101 \pm 1.5$	$1.71 \times 101 \pm 1.40$	$1.75 \times 101 \pm 1.4$	$1.44 \times 101 \pm 1.2$

Figure 12 shows the ecotoxicity tests of control brick filtrate, 1% EMS, 5% EMS, 10% EMS and 20% EMS bricks. The ecotoxicity test of the eluate was performed with *Vibrio fischeri* bacteria. The ecotoxicity tests were performed to determine the possible harmful effects of the modified stones on the environment through the release of certain elements contained in EMS or the formation of organic products. EC₅₀ values are the concentration of a substance that results in a 50% adverse effect on test organisms. The lower the EC₅₀ value, the higher the harmful effect. The results of the filtrate ecotoxicity test show that with an increase in the percentage of EMS in the bricks, the inhibition value (INH) of the aqueous phase decreases, i.e., the ecotoxicity of the aqueous eluate increases. The EC₅₀ value of the control brick was 35.72%, for bricks with 1% EMS additive 43.31%, with 5% EMS additive 39.34%, with 10% EMS additive 35.96%, while for bricks with 20% EMS, it was 33.34%. The high EC₅₀ values measured when part of the clay was replaced by EMS indicate that its ecotoxic influence is negligible [68–70].

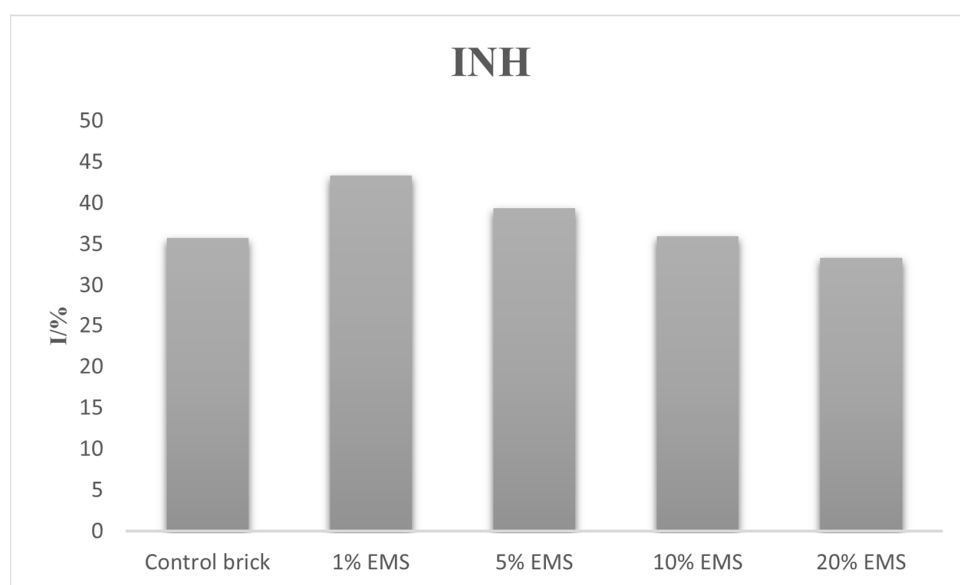


Figure 12. Ecotoxicity of prepared brick eluate in control, 1% EMS, 5% EMS, 10% EMS and 20% EMS incorporated brick.

4. Conclusions

In this work, the possibility of utilizing sludge produced during the electrochemical treatment of oily wastewater from a wet scrubber (EMS) was investigated. The electrochemical sludge was dried conventionally and then substituted in various mass ratios of 1%, 5%, 10% and 20% for part of the clay in the production of bricks. The results of the EMS and clay tests, oxide content, particle size distribution, SEM morphology and element content show the potential application of EMS in the manufacture of bricks, where the ratio of clay and non-clay raw materials needs to be optimized to achieve the desired properties.

Laboratory bricks were produced with different amounts of EMS to determine possible changes during the dehydrating and firing process, with all bricks meeting the criteria for shape, size and breaking strength.

The weight loss during the firing of the bricks increased with the percentage of EMS and the results were within the prescribed standards. Sintering bricks with EMS resulted in glassy phases and the presence of spherical pores, which can affect the mechanical properties. An increase in the percentage of EMS additive leads to a decrease in compressive strength and an increase in water absorption during firing. The results indicate an increased porosity of the bricks with a higher proportion of EMS.

The concentration of the elements was measured in all bricks. Particular attention was paid to the elements contained in the structure of stainless steel, iron and aluminium. In the bricks produced, there was a slight increase in the concentrations of Cr, Mn and Zn, which is an effect of the use of the electrodes mentioned.

The toxicity of the brick filtrate was analyzed using *Vibrio fischeri* ecotoxicity tests and the results showed an increased toxicity of the aqueous eluate with increasing EMS content. The obtained results of EC₅₀ values show that the toxic influence of EMS in bricks is negligible.

In general, the bricks in which part of the clay was replaced by EMS showed promising properties for brick production in terms of shape, size, weight loss, water absorption and compressive strength. In addition, further investigation is required on the influence of the spherical pores on the mechanical properties and the increasing toxicity of the aqueous eluate to ensure their suitability for production in brickworks.

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