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CEMENTITIOUS WASTE MATERIALS UTILIZATION IN RADIONUCLIDE IMMOBILIZATION BY SORPTION

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ABSTRACT – This paper represents an overview of the investigations of cementitious waste materials (CWM) utilization in Sr, Co, and Ni radionuclides immobilization by sorption. The highest Co^{2+} and Ni^{2+} ions removal efficiency was achieved using a wall-concrete sample, while the Sr^{2+} uptake was equal on all. The results agreed with the sorption capacity of investigated ions onto C-S-H (calcium silicate hydrate) as the main hardened cement-paste component. Studies showed that the use of CWM in the conditioning of liquid radioactive waste (LRW) could represent the efficient and economically viable alternatives for commonly used methods.

Keywords: Liquid Radioactive Waste, Concrete, Environment, Sustainable Development.

INTRODUCTION

The investigation trend of waste materials sorption characteristics has become more expressed in recent years. The utilization of waste-based materials as sorbents is highly acceptable from the aspects of environmental protection due to reduction of non-renewable resource usage, energy consumption, and generated end-waste disposal [1]. Further, the re-use of waste materials contributes to a reduction of possible environmental pollution, occupation of large surface area, and disposal costs. Among these, one of the essential things is that these materials are cost-effective and easily accessible. Likewise, the recommendation to the harmonization of all processes with the so-called 3R Criteria: reduce, recycle, and re-use, as well as the principles of the Circular economy, that implies efficient utilization of materials [2] are the main reasons for such researches. Also, high costs of immobilization (conditioning), temporary storage, and final disposal of liquid radioactive waste (LRW) encourage the application of waste materials, especially those that represent the end-waste [3]. Generally, the utilization of waste-based sorbents is widely accepted from the aspects of sustainable development.

Recent studies on cementitious waste materials (CWM) include a wide range of waste concrete, façade materials, mortar, and mixtures. The basis for these scientific researches represents the fact that these waste materials have substantial similarities with the common composite materials, i.e., solidification matrices for immobilization of LRW, such as concrete and mortar [4].

This paper presents an overview of the large part of the investigations during 2016 – 2020 of construction and demolition waste (C&DW) utilization in Sr, Co, and Ni

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radionuclides immobilization [5-10]. Studies have been shown that the usage of CWM in the sorption process could be very efficient and economically viable alternatives for standardly used methods. Since radioactive isotopes of Sr, Co, and Ni are significant components of LRW, immobilization of their ions from aqueous solutions was studied in batch sorption systems.

EXPERIMENTAL METHOD

The CWM samples were collected from five demolition sites located in the residential area of Belgrade, Serbia. Three waste cement-based sample types from the 1970s debris were used [5,6]:

- C1 – Waste concrete (walls construction),
- C2 – Waste concrete (pathways parts), and
- F – Façade waste material (from residential buildings).

Collected samples of each type were mixed, and the total amount of 1 kg was crushed, homogenized, milled, and sieved to a particle size between 0.3 and 0.6 mm to obtain representative samples (Figure 1). Three mixtures were spread over the 1 m^2 area, and 50 g per each was taken randomly from different points. Prior to the experiments, samples were washed with distilled water and dried at 373 K.

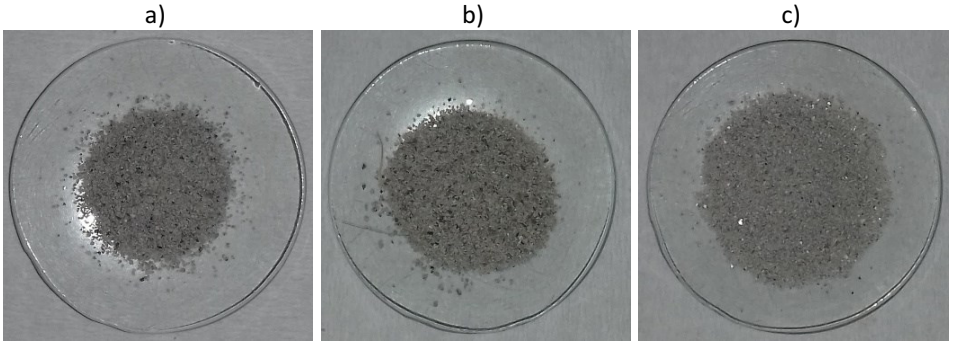

Figure 1 Prepared CWM samples: a) C1, b) C2, and C) F [7]

Sorption affinities of selected C&DW components were investigated using single-metal solutions with increasing initial metal concentration. Solutions of the specified concentration were prepared by dissolving the adequate masses of Sr^{2+}, Co^{2+}, and Ni^{2+} nitrate salts in distilled water. The initial cation concentrations were varied in the range 10^{-4} to $8 \cdot 10^{-3}$ mol/L. Sorption equilibrium was achieved by contacting 0.1 g of sorbent with 20 mL of a solution on a rotary shaker at 10 rpm, and ambient temperature for 24 h. The preliminary experiments showed that 24 h of contact time was sufficient to achieve sorption equilibrium under specified experimental conditions. Investigated solutions had natural pH between 5.0 and 5.6, and they were applied without adjustments.

The affinity of CWM to bind Sr^{2+}, Co^{2+}, and Ni^{2+} ions was defined based on sorption isotherms, i.e., the relationships between sorbed amounts of pollutants (Q_e) and residual concentrations in a liquid phase (C_e), at equilibrium. The concentrations of Sr^{2+}, Co^{2+}, and

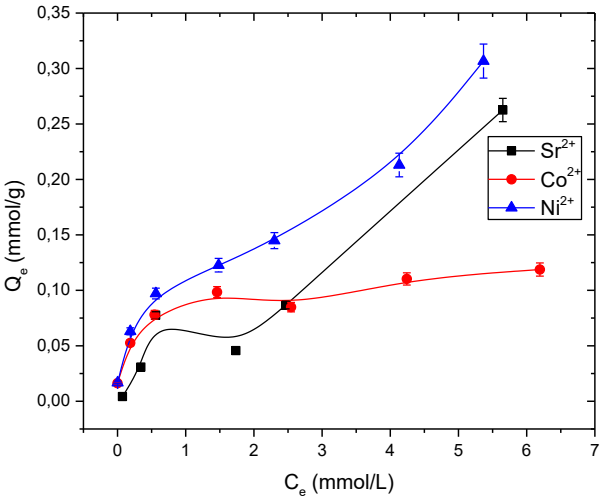

Figure 4 Sorption isotherms of Sr^{2+}, Co^{2+}, and Ni^{2+} ions onto F sample [5,7]

All samples have shown a significant affinity for sorption of Sr^{2+} cations, with an equivalent capacity of approximately 0.25 mmol/g [5-7]. Since the sorption process was followed by a linear dependence, the maximum sorption capacity was not reached and it could be expected to gain a higher value with increasing of initial cation concentrations. However, the obtained results agree with the sorption capacity of Sr^{2+} ions onto C-S-H (calcium silicate hydrate) that are the main components of hardened cement paste [11-13]. Also, the substantial sorption capacity of concrete and façade toward Sr^{2+} ions can be associated with their carbonate content [5].

The highest efficiency of Co^{2+} ions binding was achieved using samples C1 and C2 (0.32 and 0.27 mmol/g, respectively) [5-7]. The sorption capacity of Co^{2+} ions for sample F was found to be 0.12 mmol/g [5-7]. The most effective sorption of Ni^{2+} ions was onto the C1 and F samples, with a sorption capacity of 0.55 and 0.30 mmol/g, respectively. However, sample C2 showed significantly lower sorption with a maximum sorbed amount of 0.13 mmol/g [5-7]. The obtained results are in accordance with the high sorption capacities of C-S-H material according to the radioactive Co^{2+} and Ni^{2+} ions [11,12]. It might be presumed that Co^{2+} and Ni^{2+} ions sorption was the most effective onto cement-based samples, due to high equilibrium pH values [5].

Generally, the highest Co^{2+} and Ni^{2+} ions removal efficiencies were achieved using concrete sample C1, while the Sr^{2+} uptake was equal on all samples. Thus, CWM showed satisfactory performance in radionuclide removal. This feature might be primarily related to the alkaline reaction of CWM in water, which provokes dissociation of protonated surface groups, the increase in the negative surface charge, and facilitates the cation removal by precipitation in some cases [14].

Taking into account chemical compatibility with mixtures commonly used for the solidification of LRW and expressed a high affinity for studied cations, CWM has shown great potential and possibilities for further research, e.g. modification of sorbents and, in particular, the variation of experimental conditions. Also, the recent studies on Sr^{2+},

Co^{2+}, and Ni^{2+} removal by various C&DW components such as bricks, ceramic and roof tiles, and asphalt pavements relative to concrete and façade materials have indicated the highest sorption affinity of cement-based materials [5-7,9]. The sorbents of this type could very effectively replace the more expensive natural or artificially synthesized sorbent materials for radioactive isotopes from LRW.

CONCLUSION

In the present study, the suitability of CWM as a sorbent for the solidification of LRW was presented, through the sorption potential of common radioactive contaminants.

The alkaline nature and mineral composition of CWM proved to be a solid foundation for Sr^{2+}, Co^{2+}, and Ni^{2+} ions immobilization, although the highest Co^{2+} and Ni^{2+} ions removal efficiencies were achieved using old wall concrete (sample C1). Out of investigated species, Sr^{2+} ions exhibited the least effective sorption capacity. The satisfactory results were obtained using CWM due to the favorable mineral composition and alkalinity. The chemical compatibility of CWM with LRW solidification matrices must be emphasized as an advantage over natural or artificial high-capacity sorbents, which use might be environmentally inappropriate. The further removal efficiency of radionuclides testing from the real LRW in order to optimize the process conditions should be the focus of future research.

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