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IMMOBILIZATION OF ^{60}Co AND ^{90}Sr IONS USING RED MUD FROM ALUMINUM INDUSTRY

by

Aleksandra S. MILENKOVIĆ [1], *Ivana D. SMIČIKLAS* [1*],
Jelena P. MARKOVIĆ [1], *and Nikola S. VUKELIĆ* [2]

[1]Vinča Institute of Nuclear Sciences, University of Belgrade, Belgrade, Serbia
[2]Faculty of Physical Chemistry, University of Belgrade, Belgrade, Serbia

The removal of ^{60}Co and ^{90}Sr from the aqueous phase was tested using red mud – the fine grained residue from bauxite ore processing. This industrial waste represents a mixture of numerous minerals, mainly oxides and hydroxides of Fe, Al, Si, and Ti. Experiments were conducted as a function of contact time, pH, and pollutant concentrations. Kinetic data were well fitted with a pseudo-second order equation. The calculated rate constants and initial sorption rates indicated faster sorption of Sr^{2+} ions. Removal of both cations rapidly increased with the initial pH increase from 2.5 to 3.5. With the further increase of pH, Co^{2+} sorption was nearly constant (98%-100%), whereas Sr^{2+} removal remained at the same level to initial pH 8 and gradually increased to 100% at pH 12. Equilibrium sorption data followed the Langmuir model, with the maximum sorption capacities of 0.52 mmol/g for Co^{2+} and 0.31 mmol/g for Sr^{2+}. Sorbed cations exhibited high stability in distilled water. Desorption of Co^{2+} was also negligible in the presence of the competing Ca^{2+} cation, while 42%-25% of Sr^{2+} ions were desorbed depending on the previously sorbed amount. The results indicate that red mud is of potential significance as Co^{2+} and Sr^{2+} immobilization agent due to its high efficiency, abundance, and low-cost.

Key words: ^{90}Sr, ^{60}Co, immobilization, red mud

INTRODUCTION

The liquid radioactive waste, containing a variety of radioactive isotopes, arises from the regular operation of nuclear power plants. In addition, accidental releases, dismantlement of instruments containing radioisotopes and above ground nuclear testing, also contribute to the release of radioisotopes. The contaminated liquids are commonly treated by filtration, precipitation, sorption, ion exchange, evaporation, membrane separation, *etc.* [1]. Among the radioactive metals, typically present in liquid radioactive waste, ^{60}Co and ^{90}Sr are important ones. ^{60}Co is one of the corrosion products generated by neutron activation of structural materials in nuclear reactors. Nearly all of the long-lived activity in the coolant is due to ^{59}Fe, ^{99}Mo, and ^{60}Co, furthermore, activity of the ^{60}Co predominates in the post-shutdown period [2]. On the other hand, ^{90}Sr is commonly produced as a fission by-product of uranium and plutonium in nuclear power plants and research reactors [3]. While ^{60}Co is a strong gamma emitter, ^{90}Sr undergoes β^- decay.

The increasing problem of radioactive pollution results in continuous development of new and/or improved materials and methods for liquid radioactive waste treatment. Sorption by variety of inorganic and organic materials is acknowledged as one of the simple and effective methods. These processes are especially economical if naturally occurring materials, by-products and waste from various industries, can be applied as sorbents [4]. As sorbents for Co and Sr cations, a variety of materials have been tested, such as activated carbon [5], ion exchange resins [6], bentonite [7, 8], zeolite [9, 10], titanium oxide [11], synthesized inorganic ion exchangers [12], tobermorite [13], hydroxyapatite [14,15], sepiolite [16,17], *etc.* One of the industrial wastes which gained a lot of attention over the last decades is the so called "red mud", an alkaline residue of alumina production following the Bayer process [18]. After alkaline digestion of bauxite ore remaining components together with some newly formed compounds ending up in red mud, therefore, its composition is extremely heterogeneous in which Fe, Al, Si, and Ti oxides and hydroxides prevail. This residue is extremely fine in terms of particle size and strongly alkaline with the average reported pH of

* Corresponding author; e-mail: ivanat@vinca.rs

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10-13 [19]. Under such pH conditions, red mud particles carry a negative surface charge due to ionization of surface hydroxyl groups, and represent a good matrix for the sorption of cationic pollutants. Great efforts have been put into development of novel strategies for red mud utilization, with the removal of pollutants from water solutions being among the most interesting [18, 20, 21]. However, only a few studies can be found in the literature regarding red mud utilization for ^{60}Co and ^{90}Sr ions immobilization [22, 23]. The fact that it can be easily solidified in cementitious or geopolymer matrixes [24, 25] make it even more interesting for consideration in radioactive waste management.

In the present study, red mud from the "Birač" Alumina Factory (Bosnia and Herzegovina) was preliminarily tested as ^{60}Co and ^{90}Sr immobilization agent. Dried and powdered red mud was applied without the pretreatment steps (such as washing, chemical, thermal or combined treatments), in order to apply its original high alkalinity favorable for cation removal and to lower its preparation costs. The goal of the study was an evaluation and comparison of red mud efficiency for Co^{2+} and Sr^{2+} removal under various contact times, initial pH values and cation concentrations. Leaching of cations from variously loaded sorbents was tested as well, in order to explore the stability of obtained products.

MATERIALS AND METHODS

Red mud sorbent

The red mud was separated from the excess alkaline liquor by decanting and dried at 105 °C. Prior to experimental work, the dried residue was powdered and homogenized with a mortar and pestle.

Chemical analysis of the sample showed that it consists of Fe_2O_3 (42.42%), Al_2O_3 (18.08%), SiO_2 (12.62%), TiO_2 (4.63%), CaO (2.86%), Na_2O (8.92%), and the loss of ignition was 7.93% [26]. In the XRD spectra, hematite (Fe_2O_3), gibbsite and bayerite ($Al(OH)_3$), quartz (SiO_2), sodalite ($Na_8Si_6Al_6O_{24}Cl_2$), calcite ($CaCO_3$), and both anatase and rutile (TiO_2), were identified as main crystalline phases [26].

Sorption experiments

As the substitutes for radioactive ^{60}Co and ^{90}Sr ions, inactive nitrate salts of analytical purity were used ($Co(NO_3)_2$ $6H_2O$, and $Sr(NO_3)_2$). The sorption experiments were carried out in closed PVC bottles, by agitating suspensions containing 0.1 g of sorbent and 20 mL of appropriate solution (solid to solution ratio 1:200). The separate batches were agitated on a horizontal laboratory shaker at room temperature (20 1 °C). Variously concentrated KOH and HNO_3 solu-

tions were used for the adjustment of initial pH values, using the InoLab WTW pH-meter. After specified time intervals, the solid residues were separated from the liquid phase by centrifugation and filtration. The final solution pH values were measured.

The amounts of Co^{2+} and Sr^{2+} ions removed from the aqueous phase were calculated as differences between the initial concentrations in working solutions and the residual metal concentrations after contact with the sorbent. Cation concentrations were determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), using the ICP Perkin Elmer Plasma 400 instrument. The working wavelengths were 238.892 nm and 407.771 nm for Co^{2+} and Sr^{2+}, respectively, whereas the estimated detection limit was 0.1 mg/L for both cations.

The influence of contact time

The effect of contact time on the amount of cations removed was determined by equilibrating the red mud with 2 10^{-3} mol/L Co^{2+} and Sr^{2+} solutions, at an initial pH 5. Nine identical batches for each system were prepared and placed on the shaker. At different time intervals (from 5 min to 48 h) one of the batches was taken for solid/liquid separation. In order to monitor the pH changes in the absence of Co^{2+} and Sr^{2+}, the blank experiment was also performed using distilled water at initial pH 5.

The influence of solution pH

The effect of pH on Co^{2+} and Sr^{2+} sorption by red mud was screened using a solution with constant initial cation concentration (2 10^{-3} mol/L) and variable pH, adjusted in the wide range from 2.5 to 12. Based on the results of kinetic experiments, the contact time was set at 48 h, to assure equilibrium conditions. The blank experiment, with distilled water at different initial pH, was also performed.

The influence of initial Co^{2+} and Sr^{2+} concentrations

The effect of the initial cation concentration was analyzed in the Co^{2+} and Sr^{2+} concentration range from 10^{-4} to 10^{-3} mol/L. Initial pH value of each batch was adjusted to 5 prior to sorbent addition. Residual cation concentrations and equilibrium pH values were determined after 48 h of contact time.

Desorption of Co^{2+} and Sr^{2+}

Variously loaded sorbents obtained after the experiment presented in the previous section were dried at 105 °C, and submitted for sequential extraction. Residues were firstly equilibrated with 20 mL of dis-

tilled water, and subsequently with 20 mL of 0.5 mol/L Ca(NO$_3$)$_2$ solution at pH 6. Suspensions were shaken for 24 h. Leached metal concentrations and final pH values were measured after each step.

RESULTS

Co^{2+} and Sr^{2+} sorption experiments

Effect of contact time

The amounts of Co^{2+} and Sr^{2+} sorbed at various time intervals are presented in the fig. 1(a). Both cations exhibited two-step sorption kinetics onto red mud: a rapid initial step in the first 6 h of contact, followed by the slower sorption of Co^{2+} and Sr^{2+} ions in the next 42 h. Sorption of Sr^{2+} ions was faster than Co^{2+} at the process beginning and the equilibrium was reached after 24 h. On the other hand, amounts of immobilized Co^{2+} increased slightly during the second
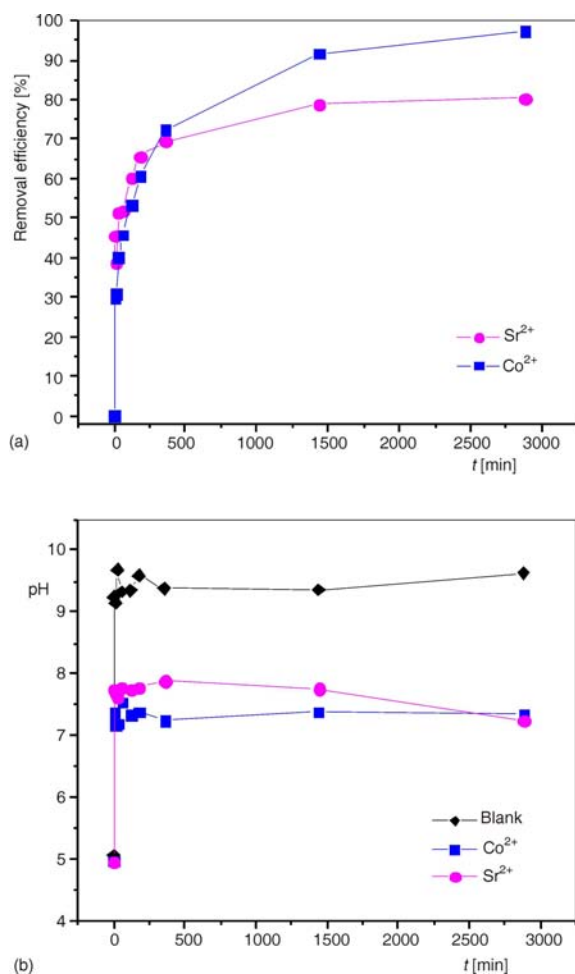
day of equilibration. Red mud separated Co^{2+} ions from the solution more efficiently than Sr^{2+} (97% and 79%, respectively, at equilibrium).

Changes of pH, monitored during the course of the reaction, are presented in fig. 1(b). In the absence of investigated cations, pH rapidly increased from initial pH 5 to above 9, and with the slight fluctuations remained at pH ~9.5 in the studied time interval. Since the sorbent was prepared without prior washing or neutralization, high pH values are principally due to the presence of NaOH added in the Bayer process. Although instantaneous pH increase was also noticed using Co^{2+} and Sr^{2+} solutions, final pH values were considerably lower than in the blanks. Somewhat higher pH values were detected for Sr^{2+} containing solutions at shorter contact times, but at the end of the process comparable equilibrium pH values of ~7.2 were obtained for both cations. The experimental data were fitted using a pseudo-second order equation [27], in the following linear form

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (1)$$

where k_2 [gmmol^{-1}min^{-1}] is the pseudo-second order rate constant, q_e [mmol g^{-1}] – the amount of Co^{2+} or Sr^{2+} sorbed at equilibrium, and q_t – the amount of cation sorbed at any time t. After linear fitting and determination of k_2 and q_e, the initial sorption rates h [mg g^{-1} min^{-1}], were calculated when $t \to 0$, using equation

$$h = k_2 q_e^2 \qquad (2)$$

The results of linear fitting and calculated kinetic parameters are presented in fig. 2, and tab. 1.

High correlation coefficients (R^2) suggest good agreement between experimental data and the theoretical model. Likewise, the q_e values calculated by eq. 1 are close to the ones determined experimentally.
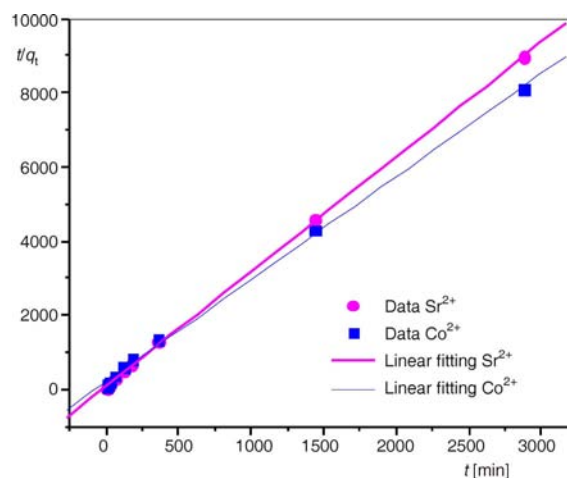

Figure 1. Effect of contact time between red mud and Co^{2+} or Sr^{2+} containing solutions (initial cation concentration 2 10^{-3} mol/L, initial pH 5, sorbent dose 0.1 g/20 mL, temperature 20 °C) on: (a) amounts of Co^{2+} and Sr^{2+} cations sorbed, (b) final solution pH values. The lines connecting data points do not represent any fitting

Figure 2. Pseudo-second order kinetic model of Co^{2+} or Sr^{2+} sorption by red mud as a function of contact time

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Table 1. Sorption kinetics parameters obtained using the pseudo-second order model

Cation	q_e [mmolg^{-1}]	[mgg^{-1}]	k_2 [g/(mmol min)]	h [mmol/(g min)]	R^2
Sr^{2+}	0.32	28.3	0.101	0.010	0.999
Co^{2+}	0.36	21.3	0.037	0.004	0.998

Effect of initial pH

The pH profile of Co^{2+} and Sr^{2+} sorption by red mud is presented in fig. 3(a). The sharp increase in sorption with the increase of pH values between 2.5 and 3.5 was common for both cations. In the initial pH range 4-8 sorption was constant (98% and 76%, respectively for Co^{2+} and Sr^{2+}). At pH >8, complete removal of Co^{2+} was achieved, whereas Sr^{2+} sorption gradually increase reaching 100% at pH 12.

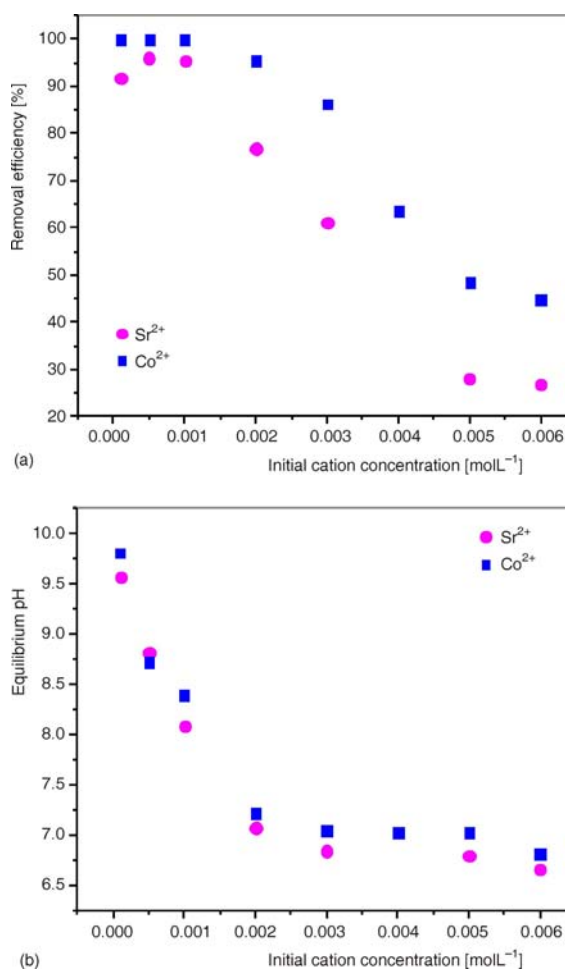From fig. 3(b) the relationships between initial and final pH values can be observed. In the blank solution, final pH values increased rapidly along with the initial ones in the narrow range 2.5-3.5. The plateau occurred in the initial range ~3.5-~10, while for the initial pH >10 final pH increased again. At the plateau, pH value of 9.5 was characteristic for the blank solution. Using Co^{2+} and Sr^{2+} containing solutions, final pH values were mutually comparable up to pH 8. However, these values were considerably lower when compared to the blanks. For the initial pH >8, the final pH increased more rapidly in Co^{2+} solutions.

Effect of initial Co^{2+} and Sr^{2+} concentrations

Removal efficiencies of Sr^{2+} and Co^{2+} ions by red mud as a function of initial cation concentrations are presented in fig. 4(a). The quantities of sorbed Co^{2+} were generally higher than for Sr^{2+}. Furthermore, no detectable amounts of Co^{2+} were found after red mud contact with solutions of initial Co^{2+} concentration in the range 10^{-4}-10^{-3} mol/L. The efficiency of Co^{2+} sorption decreased from 100% to 45% when the entire investigated range of concentrations is consid-

Figure 3. Effect of initial solution pH values on:
(a) removal efficiency of Co^{2+} and Sr^{2+} cations by red mud, (b) final solution pH. Initial cation concentration 2 10^{-3} mol/L, sorbent dose 0.1 g/20 mL, contact time 48 h, temperature 20 °C. The lines connecting data points do not represent any fitting

Figure 4. Effect of initial cation concentration on:
(a) removal efficiency of Co^{2+} and Sr^{2+} cations by red mud, (b) final solution pH. Initial pH 5, sorbent dose 0.1 g/20 mL, contact time 48 h, temperature 20 °C

ered, while Sr^{2+} sorption efficiency decreased from 92% to 27%.

Increasing metal sorption provoked lower equilibrium pH values, fig. 4(b). In fig. 5(a) the isotherms of Co^{2+} and Sr^{2+} sorption are presented as the relationships between equilibrium cation concentrations in the solid and in the liquid phases. With the increase of pollutant concentration, saturation of available surface sites led to almost constant Co^{2+} and Sr^{2+} removal, defined as a maximum sorption capacity for a particular cation.

The Langmuir eq. [28], most commonly used for the description of sorption processes, was tested in the present study using the following linear form

$$\frac{C_e}{q_e} \quad \frac{1}{K_L q_m} \quad \frac{C_e}{q_m} \qquad (3)$$

where q_e [mmol g^{-1}] is the amount of metal ion sorbed at equilibrium per gram of sorbent, C_e [mmol L^{-1}] – the equilibrium concentration of metal ion in the solution , q_m and K_L the Langmuir model constants related to sorbent capacity and affinity, respectively.
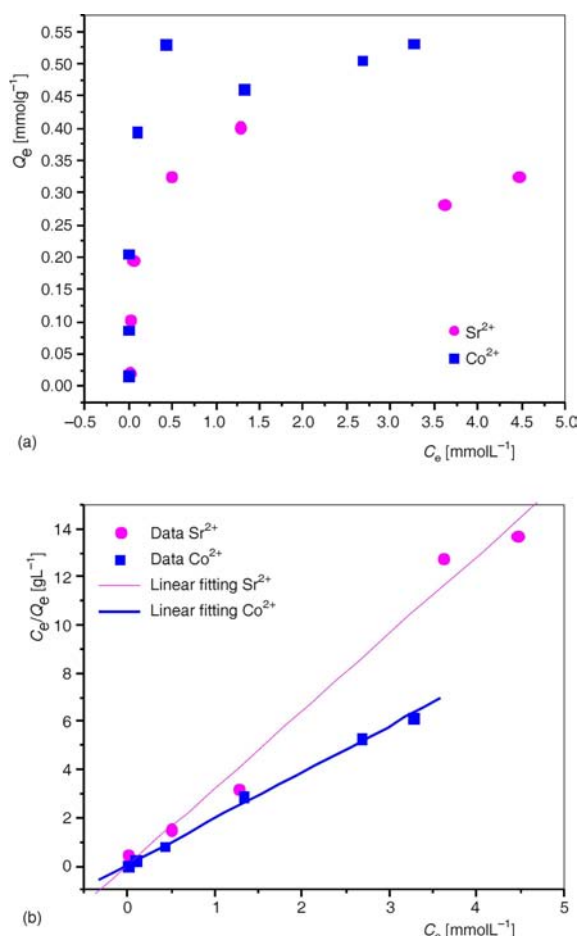
Figure 5(b) shows the results of equilibrium data fitting, whereas calculated parameters are presented in tab. 2.

The quality of the isotherm fit is typically assessed based on the magnitude of the regression coefficient. Since the R^2 values are close to unity for both metal cations, it appears that Langmuir model acceptably fit the experimental data over the investigated concentration range. At the given experimental conditions, the maximum sorption capacity of red mud was 0.52 mmol/g for Co^{2+} and 0.31 mmol/g for Sr^{2+}.

Desorption of Co^{2+} and Sr^{2+}

The results of leaching experiments are presented in fig. 6. Cobalt concentrations in the aqueous phase were below the detection limit, regardless of the

Table 2. Equilibrium sorption parameters determined by the Langmuir model

Cation	q_m		K_L	R^2
	[mmolg^{-1}]	[mgg^{-1}]	[Lmmol^{-1}]	
Sr^{2+}	0.31	27.2	91.74	0.986
Co^{2+}	0.52	30.6	41.15	0.996

(a)

(b)

Figure 5. (a) Sorption isotherms of Co^{2+} and Sr^{2+} ions on red mud. Initial pH 5, sorbent dose 0.1 g/20 mL, contact time 48 h, temperature 20 °C, (b) Experimental data fitting using the linear Langmuir equation

(a)

(b)

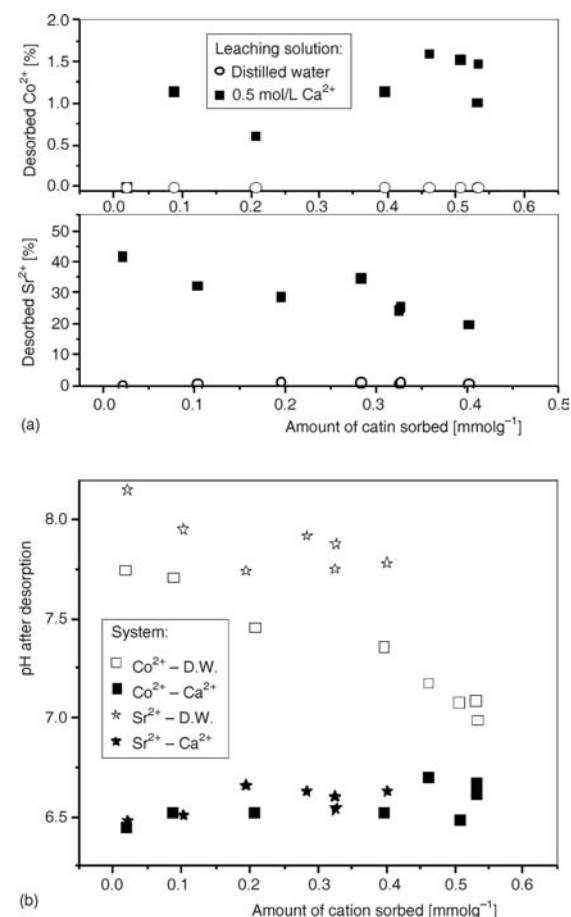**Figure 6. (a) Percentages of Co^{2+} and Sr^{2+} ions desorbed in distilled water (D. W.) and 0.5 mol/L Ca^{2+}, as a function of sorbed cation amounts, (b) pH values measured after consecutive extraction steps**

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previously sorbed quantity fig. 6(a). Moreover, Co^{2+} exhibited high stability in Ca^{2+} containing solution (maximum desorption 1.6%).

Strontium cations desorption in distilled water was also very low, *i. e.* up to 1% in relation to the previously sorbed quantity fig. 6(a). On the other hand, Ca^{2+} ions acted as strong competitors, displacing considerable amounts of Sr^{2+} back into the solution. Percentages of leached Sr^{2+} generally showed a decreasing dependence on the amount of sorbed cation (42%-25%, with increasing load).

Final pH ranges were 7.7-7.0, and 6.4-6.7, respectively, for water and Ca^{2+} containing solutions after equilibration with Co-loaded sorbents fig. 6(b). In the case of Sr-loaded sorbents, final pH values were higher or similar to the ones detected in Co-containing systems (8.1-7.9 in distilled water, 6.5-6.6 in Ca^{2+} solution).

DISCUSSION

Analysis of the results obtained under various experimental conditions enables the evaluation and comparison of red mud effectiveness for Co^{2+} and Sr^{2+} immobilization. Based on macroscopic evidence, the possible sorption mechanisms can also be proposed.

Kinetic experiments have revealed that sorption of Sr^{2+} was faster in respect to Co^{2+}, with higher calculated pseudo-second order rate constant and initial sorption rate (tab. 1). The equilibrium state was achieved more rapidly in the Sr^{2+} containing system but the equilibrium sorbed amount was lower. To our knowledge, there is no comparative study of Co^{2+} and Sr^{2+} sorption kinetics on the same red mud sample. In the work of Apak *et al.* [22], Sr^{2+} sorption kinetics on variously treated red mud samples was not shown, however, it was stated that the equilibrium state was reached within 4 h under applied mixing conditions. Nadaroglu and Kalkan [23] found that Co^{2+} sorption onto washed and subsequently acid activated red mud reached its maximum after 15 min of contact and then decreased, but no explanation of this phenomenon has been offered.

In our study, solution pH rose rapidly at the beginning of the process but it is important to notice that pH values were by approximately 2 pH units lower compared to the blank solution at any specified time interval, fig. 1(b). pH decrease related to cation sorption indicates a release of protons either by ligand exchange (sorbing cation replaces the protons on the surface of the sorbent, eqs. 4 and 5) or by hydrolysis reactions, when protons are released from the hydration sphere of aqueous cations prior or during the sorption (eqs. 6 and 7) [29]

$$XOH + M^2 \rightarrow XOM + H \qquad (4)$$

$$2XOH + M^2 \rightarrow (XO)_2M + 2H \qquad (5)$$

$$M^2 + H_2O \rightarrow M(OH) + H \qquad (6)$$

$$M^2 + 2H_2O \rightarrow M(OH)_2 + 2H \qquad (7)$$

where X denotes structural cation such as Fe, Al, Si, Ti, *etc.*

In aqueous solutions at concentrations of less than 0.1 mol/L, divalent cobalt is present dominantly as the hexaaquo complex Co(H$_2$O)$_6^2$ at pH < 8, while at higher pH principally in the form of hydrolysis products [30]. Precipitation of Co(OH)$_2$ starts at pH ~8 [14, 31]. On the other hand, divalent strontium is typically co-ordinated by 8 water molecules [29] and it is not susceptible to hydrolysis under a range of pH used in this study [31]. Considering that time dependant final pH values were <8, replacement of surface H$^+$ ions by sorbing metal cations is likely to occur (eqs. 4 and 5).

The increase of initial pH led to higher removal efficiencies, fig. 3(a). In the acidic pH region, sorption by red mud is generally suppressed by the presence of competing H$^+$ ions, as well as by dissolution of the sorbent constituents such as sodalite and calcite, and the overall positive surface charge [32]. Strontium immobilization was more affected in acidic media, *i. e.* the removal efficiency at initial pH 2.5 was 9% for Sr^{2+} while 38% for Co^{2+} ions. The neutralization capacity of untreated red mud was demonstrated by a significant increase of acidic initial pH values to near neutral or neutral equilibrium pH, fig. 3(b). For comparison, washed and acid treated red mud from Turkey exhibited low Co^{2+} sorption efficiency in the acidic media (up to 12% at initial pH 3) [23], as a result of neutralization and partial dissolution of major buffering minerals during the treatment.

In the initial pH range 4-8, buffering effect of red mud led to the constant final pH values and consequential constant amounts of Co^{2+} removed from the solution, fig. 3(a). Considering pH dependant Co^{2+} speciation, sorption of Co(OH)$^+$ and precipitation of insoluble Co(OH)$_2$ are likely to occur at pH > 8. Improved Sr^{2+} immobilization in the region of alkaline initial pH correlates with the rise of equilibrium pH, *i. e.* with the progressive dissociation of surface hydroxyl groups and development of negative surface charge [18, 20].

The values of maximum sorption capacities (tab. 2) imply higher affinity of the sorbent towards Co^{2+} ions. This is in agreement with the general observation that equilibrium constants for cation sorption and quantities of specifically sorbed ions onto the hydrous metal oxide surfaces are correlated with the first hydrolysis constants of the cations, as well as with their ionic potentials (defined as the square of the cation charge divided by the radius of the cation, Z^2/r) [29]. The lower value of the first hydrolysis constant (logK$_{CoOH}$ = 9.6 and logK$_{SrOH}$ = 13.3) and the higher ionic potential (4.55 and 3.03 for Co^{2+} and Sr^{2+}, re-

spectively) indicate the higher tendency of Co^{2+} to form inner-sphere surface complexes.

The shape of the isotherm provides some basic information about the nature of the sorbent surface and the sorbate interactions. Giles *et al.* [33] have classified solute adsorption isotherms into four main types primarily by their initial shape and slope: Langmuir (L)-type with an initial concavity to the concentration axis, H-type with an apparent intercept on the ordinate, S-type with an initial convexing to the concentration axis, and C-type with an initial linear portion. In the studied concentration range, the Sr^{2+} isotherm belongs to the L-group, fig. 5(a). The ratio between the concentration of the cation remaining in solution and sorbed on the solid decreased with the increase of cation concentration, leading to a progressive saturation of the red mud. On the other hand, Co^{2+} sorption isotherm can be assigned to the H-group (high affinity), characterized by the total removal of the solute from the solutions of different initial concentrations. Extremely strong sorption in the lower concentration range is a result of the surface complexation mechanism of the inner-sphere type and/or the sorbate precipitation. In our study, for lower Co^{2+} concentrations (10^{-4}-10^{-3} mol/L) red mud alkalinity caused final pH values above Co(OH)$_2$ precipitation threshold, therefore the Co^{2+} removal from the aqueous phase can be related to the precipitation of insoluble hydroxide.

Desorption tests were conducted to explore the stability of obtained products, which is an important issue from the aspects of spent sorbent handling and disposal. Furthermore, the results can support the conclusions about the main sorption mechanisms. The amount of cations leached in the water solution was negligible, fig. 6(a). The pH values measured after the first desorption step were in the range of 7-8, fig. 6(b), thus the caustic nature of red mud played an important role in terms of sorbed metal stability. Furthermore, sorbed Co^{2+} cannot be easily released by coexisting Ca^{2+} ions and increased ionic strength of the surrounding medium. This confirms that inner-sphere complex

formation and/or precipitation/co-precipitation are dominant mechanisms of Co^{2+} immobilization by red mud. The amount of desorbed Sr^{2+} was affected by the presence of Ca^{2+}, which signifies that a fraction of the total sorbed amount was attached to the solid surface by relatively weak electrostatic interactions and the ion-exchange mechanism. Nevertheless, a large amount of Sr^{2+} (58%-75%, depending on the initially sorbed quantity) was retained by stronger bonds, most likely by specific cation sorption, *i. e.* inner-sphere complex formation. This is in agreement with the results of Sr^{2+} sorption experiments performed using washed, acid treated and heat treated red mud samples, which indicated that the primary mode of Sr^{2+} sorption onto red mud was specific sorption while the secondary mode was ion-exchange [22]. It was observed that the red mud sorption capacity was reduced after the heat treatment, and given that high temperature was detrimental for – SOH surface sites, these sites were recognized as the most responsible for high Sr^{2+} affinity. Conclusions about sorption mechanisms have to be verified, particularly on the microscopic level utilizing instrumental analyses.

Capacities of some mineral and waste derived sorbents are summarized in tab. 3.

The maximum amounts of Co^{2+} and Sr^{2+} sorbed per gram of added red mud are higher in respect to the values reported for naturally occurring minerals (clinoptilolite, bentonite, sepiolite, montmorillonite) and synthetic hydroxyapatite, at similar initial pH (5-6). The red mud from Turkey, applied after washing and acid activation, exhibited the capacity of 31.05 mg/g (0.53 mmol/g) for Co^{2+} at pH 5.5, which is comparable to the value obtained in this study. Tobermorite derived from newsprint recycling combustion ash exhibited capacities lower than red mud, however it should be noted that the working initial pH was 1. On the other hand, zeolite derived from fly ash exhibited substantially higher capacities for both cations even at lower pH (3.5). Utilization of abundant mining and industrial by-products is beneficial

Table 3. Maximum sorption capacities of some mineral and waste derived sorbents

Sorbent	Cation	Initial pH	q_m [mmolg^{-1}]	[Ref.]
Clinoptilolite	Sr^{2+} Co^{2+}	5	0.11 0.05	[10]
Bentonite	Co^{2+}	5	0.14	[34]
Sepiolite	Sr^{2+} Co^{2+}	5.6	0.20 ~0.25	[16] [17]
Montmorillonite	Sr^{2+} Co^{2+}	6.0	0.19 0.27	[31]
Hydroxyapatite	Sr^{2+} Co^{2+}	5.0 5.0	0.25 0.35	[15] [14]
Waste derived tobermorite	Sr^{2+} Co^{2+}	1.0	0.017 0.117	[13]
Zeolite derived from fly ash	Co^{2+}	3.5	1.597-1.871	[35]
Red mud washed/acid treated	Co^{2+}	5.5	0.53	[23]
Red mud	Sr^{2+} Co^{2+}	5.0	0.31 0.52	This study

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in respect to sorbents obtained by mineral excavation or synthetic routes, due to economic feasibility and waste reduction. Considering the fact that the red mud was applied without treatment or activation steps, capacities for Co^{2+} and Sr^{2+} immobilization are promising.

CONCLUSIONS

The possibility of red mud revalorization was tested, through its application as a sorbent for radioactive contaminants ^{60}Co and ^{90}Sr. The cation removal from aqueous media was studied in batch conditions by varying the major process parameters. Red mud exhibited high removal efficiencies over a range of experimental conditions. Compared to Co^{2+}, sorption of Sr^{2+} ions was found to be faster and more sensitive to acidic media. The maximum sorption capacities of 0.31 mmol/g for Sr^{2+} and 0.52 mmol/g for Co^{2+} were obtained. Cation sorption was followed by a substantial decrease of solution pH in comparison with the blank solutions. Spent sorbents loaded with different amounts of cations exhibited high stability in distilled water, while in the Ca^{2+} containing solutions Sr^{2+} desorption was pronounced. Taking into consideration experimental results from both sorption and desorption experiments, as well as pH dependant cation speciation, it can be proposed that immobilization of Co^{2+} took place mainly by formation of inner-sphere surface complexes and $Co(OH)_2$ precipitation. Sr^{2+} removal from aqueous phase occurred primarily by specific sorption mechanisms, whereas ion-exchange and electrostatic interactions are indicated as bonding mechanisms of secondary significance. Red mud capacity for the removal of Co^{2+} and Sr^{2+} was higher in respect to the performance of many naturally occurring mineral sorbents. The results indicate that red mud is of potential significance as Co^{2+} and Sr^{2+} immobilization agent due to its high efficiency, abundance and low-cost.

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AUTHOR CONTRIBUTIONS

The literature search and study design was carried out by A. S. Milenković and I. D. Smičiklas. Experiments were done by A. S. Milenković, whereas analytical measurements were carried out by J. P. Marković. All authors participated in the analysis and discussion of the results. Writing the manuscript was done by A. S. Milenković, I. D. Smičiklas, and N. S. Vukelić.

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Александра С. МИЛЕНКОВИЋ, Ивана Д. СМИЧИКЛАС,
Јелена П. МАРКОВИЋ, Никола С. ВУКЕЛИЋ

ИМОБИЛИЗАЦИЈА ЈОНА [60]Co И [90]Sr УПОТРЕБОМ ЦРВЕНОГ МУЉА ИЗ ИНДУСТРИЈЕ АЛУМИНИЈУМА

Испитана је могућност уклањања јона [60]Co и [90]Sr из течне фазе помоћу црвеног муља – ситнозрног отпадног материјала који настаје прерадом руде боксита. Овај индустријски отпад представља смешу више минералних врста, углавном оксида и хидроксида Fe, Al, Si и Ti. Експерименти су спроведени у функцији времена контакта, pH и концентрације загађивача. Резултати кинетичких експеримената су добро фитовани једначином псеудо-другог реда. Израчунате вредности константе брзине реакције и иницијалне брзине сорпције указују на бржу сорпцију јона Sr^{2+}. Уклањање оба катјона скоковито расте са порастом иницијалне pH вредности у опсегу од 2.5 до 3.5. Са даљим порастом pH вредности, сорпција Co^{2+} јона је уједначена (98% -100%), док је уклањање јона Sr^{2+} константно до pH 8, а затим постепено расте достижући 100% на pH 12. Резултати добијени за сорпцију у равнотежним условима се могу добро описати Лангмуировим моделом, са максималним сорпционим капацитетима од 0.52 mmol/g за Co^{2+} и 0.31 mmol/g за Sr^{2+}. Сорбовани катјони су показали високу стабилност у дестилованој води. Десорпција Co^{2+} јона је веома ниска и у раствору компетитивних Ca^{2+} јона, а количина десорбованих Sr^{2+} јона варира од 42% до 25% у зависности од претходно сорбоване количине. Добијени резултати указују на потенцијални значај црвеног муља као имобилизационог агенса за јоне Co^{2+} и Sr^{2+}, захваљујући високој ефикасности, распрострањености и ниској цени.

Кључне речи: [90]Sr, ^{60}Co, имобилизација, црвени муљ