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# The use of composite ferrocyanide materials for treatment of high salinity liquid radioactive wastes rich in cesium isotopes

**Abstract:** The use of composite materials based on metal ferrocyanides combined with natural mineral sorbents for treatment of high salinity Cs-containing liquid radioactive waste (LRW) was investigated. The study indicated that among the investigated composites, the best sorption characteristics for Cs were shown by materials based on copper ferrocyanide. Several factors affecting the removal of cesium from LRW, namely total salt content, pH and organic matter content, were also investigated. High concentrations of complexing organic matter significantly reduced the sorption capacity of ferrocyanide sorbents.

**Keywords:** Cesium, Liquid radioactive wastes, Composite, Ferrocyanide.

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## 1 Introduction

Liquid radioactive wastes (LRW) from nuclear facilities constitute a key nuclear legacy issue globally. The IAEA estimate a global cumulative high level waste (HLW) inventory of 34 000 m<sup>3</sup> ( $4.2 \times 10^7$  TBq) from nuclear power generation and 800 000 m<sup>3</sup> ( $3.1 \times 10^7$  TBq) from defense and weapon-related activities, mostly stored in liquid form [1]. These wastes require careful management and processing to reduce the risk of accidental discharge, stabilize and/or reduce the volume of the waste, and ultimately allow safe disposal [2].

Currently, the former Fast Breeder reactor BN-350 in Aktau, Kazakhstan (which operated between 1973 and 1999) is being decommissioned. The nuclear power complex in Mangistau stores about 5000 m<sup>3</sup> of liquid radioac-

tive waste (LRW) produced over the lifetime of the reactor. This LRW has a total volume activity of  $10^7$ – $10^8$  Bq L<sup>-1</sup>. The waste storage tanks currently provide a stable repository for the LRW [3]. However, the LRW with its high salt content can in the long term corrode the structural materials of these tanks, and this poses serious potential environmental risks in the vicinity of the facility.

In international practice, selecting the most appropriate method for managing LRW is determined by technical and non-technical factors. The most frequently used treatment techniques include micro-ultrafiltration using ceramic filters, reverse osmosis and selective sorption on organic and inorganic materials [4]. For example, a relatively successful method employed in the LRW cooling pool at the Taiwan Research Reactor uses a cascade of ceramic filters with diatomite [5]. However, equivalent technology cannot be applied on highly mineralized LRW, which is the case for the LRW from BN-350. Similarly, it is not effective to apply processing technologies which use reverse osmosis membranes due to limitations imposed by the chemical composition and high salinity of the liquid wastes. For the processing of concentrated LRW with a high content of nitrates and borates in the Loviisa NPP (Finland) and the Paks NPP (Hungary) precipitation is used to remove borate salts followed by further purification *via* removal of cesium ions using sorbents based on cobalt ferrocyanide. Copper and nickel ferrocyanides have also been applied as separation media [6–8].

Previous research has proposed a large number of materials for the extraction of cesium and other radionuclides from LRW [2, 4, 9]. For example, recent research has targeted agricultural residues [10], pure ferrocyanides [8, 9], their polymeric composites [11, 12], nanofibers, nanofilms [13, 14], powdered activated carbon [15] *etc.* However, the proposed sorption materials have a number of deficiencies which have limited their widespread implementation in practice. In particular, untreated natural sorbents (zeolites, clays) do not have the necessary selectivity towards Cs ions (which are typically major dose contributors in LRW) or ability to retain their sorption characteristics in high salinity solutions, and so may generate large amounts of secondary waste. Pre-

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precipitates of pure ferrocyanides of heavy metals, despite their high affinity towards cesium, are soluble in alkaline solutions and are inclined to peptization. Milyutin *et al.* however note the improved sorptive performance of nickel potassium ferrocyanide in alkaline media when precipitated onto a mineral support (which these authors attributed to the formation of a nickel potassium ferrocyanide phase firmly fixed on the support surface, which is resistant to peptization) [8].

A number of authors have studied such composite sorbent materials although critical reviews [4, 9] indicate that organic-based composites are often limited in their performance for alkaline and high salinity liquid wastes.

Inorganic (mineral-based) composite sorbents however show considerable potential: their cost is typically much lower than organic polymer-based composite materials, and an inorganic porous matrix may additionally remove other radionuclides of concern such as strontium-90 and plutonium. Here, we examine and compare the performance of a range of heavy metal ferrocyanides adsorbed onto low-cost, bulk natural sorbent - mineral matrices for the extraction of cesium from highly mineralized, alkaline LRW, using simulated BN-350 reactor LRW as an example waste. Further, the sorption characteristics of these composite ferrocyanide materials are assessed under varying pH, salinity and concentrations of organic complexing agents.

## 2 Materials and methods

15 ferrocyanide composites were synthesized for study, based on copper, nickel and cobalt ferrocyanide precipitated onto five different mineral sorbents (sourced from within Kazakhstan) – zeolite from the deposit “Bagration”, clays (red clay, yellow clay and green clay) from the “Semeytau” deposits, and montmorillonite from the “Akzhar” deposit. These natural sorbents differ substantially in their mineral and chemical compositions. The zeolites are similar in mineral composition to clinoptilolite, with inclusion of other minerals (quartz, hydromica, montmorillonite and glauconite), producing the following chemical composition:  $\text{SiO}_2$  – 57.9%,  $\text{Al}_2\text{O}_3$  – 21.2%,  $\text{K}_2\text{O}$  – 3.2%,  $\text{Fe}_2\text{O}_3$  – 2.4%,  $\text{CaO}$  – 2.1%,  $\text{Na}_2\text{O}$  – 1.5%,  $\text{SO}_3$  – 0.99%. Natural clays (separated by color – red, yellow and green) represent bentonites with variable chemical composition:  $\text{SiO}_2$  – 55%–65%,  $\text{Al}_2\text{O}_3$  – 18%–23%,  $\text{Fe}_2\text{O}_3$  – 4%–8%,  $\text{CaO}$  – 2%–4%,  $\text{MgO}$  – 2%–3%,  $\text{K}_2\text{O}$  – 0.5%–1%,  $\text{Na}_2\text{O}$  – 0.5%–1%. Clay deposits from Akzhar are dominated by montmorillonite. Data on the precise chemical composition of these clays is not available.

Sorbents were synthesized as follows: a suspension of the powdered natural sorbent in the metal’s sulfate solution was prepared, and maintained to achieve balance and saturation of the sorbent metal’s ion (1 h). Then slowly, with vigorous stirring, a solution of hexacyanoferrate(II) of potassium in an equivalent amount to the metal’s ion was added. The obtained pulp was allowed to stand for an hour, then filtered, washed with distilled water, dried and ground to a smooth paste. The ratio of mineral matrix: ferrocyanide metal in the obtained samples was 1 : 1. A total of 24 sorbents were tested – 15 composites, 5 natural sorbents, 3 dry ferrocyanide samples, and 1 commercially available granulated sorbent bead based on nickel-potassium ferrocyanide containing zirconium hydroxide as a framework (Termoksid-35), which was tested for comparison.

Sorption of microquantities of cesium on composite ferrocyanide sorbents was carried out under static conditions by continuously stirring samples of air-dried sorbent with an aliquot of the liquid phase for 1 h, which was then allowed to stand for 2 h for additional capture of cesium ions. The ratio of the solid and liquid phases was 1 : 400. After standing the liquid and solid phases were separated by filtration through cellulose medium-fast filtration filter paper.

Contents of the main components of salinity and cesium were determined by atomic emission spectrometry (ICP-AES-iCAP 6300) and mass spectrometry (ICP-MS-ELAN 9000).  $^{137}\text{Cs}$  and  $^{134}\text{Cs}$  specific activities were determined by gamma-spectrometry [16, 17]. pH was monitored using a Mettler Toledo potentiometric pH meter. All experiments were performed in triplicate, with the exception of kinetic experiments which were repeated four times. Error bars in all figures show the 95% confidence interval for each data point based on these triplicate (or quadruplicate) determinations.

For modeling the effects of different parameters on the sorption of cesium (pH, salinity, organic matter content): pH was adjusted using concentrated solutions of nitric acid and sodium hydroxide; salinity was modified by varying the concentration of the main component of the waste’s salt content – sodium nitrate; and organic matter was introduced in the form of the complexants  $\text{Na}_2\text{-EDTA}$  and oxalic acid, which are used as decontaminating agents in NPP operation and which may reduce sorption efficiency.

The chemical and radionuclide composition of model solutions was as close as possible to the composition of LRW BN-350 [3] (Table 1).

The specific surface area ( $S_{\text{sp}}$ ) of the sorbents was investigated by absorption of water vapor at different satu-

**Table 1:** Composition of model solutions imitating LRW BN-350.

Parameters	Unit of measurement	Value	Parameters	Unit of measurement	Value
Dry residue	g L <sup>-1</sup>	100	Cesium	mg L <sup>-1</sup>	150
Alkalinity	mol L <sup>-1</sup>	0.1	<sup>137</sup> Cs	Bq L <sup>-1</sup>	110 ± 10
Hardness	mol L <sup>-1</sup>	0.18	<sup>134</sup> Cs	Bq L <sup>-1</sup>	460 ± 20
Sodium	g L <sup>-1</sup>	30	<sup>241</sup> Am	Bq L <sup>-1</sup>	200 ± 20
Chlorides	g L <sup>-1</sup>	15	<sup>60</sup> Co	Bq L <sup>-1</sup>	30 ± 3
Nitrates	g L <sup>-1</sup>	30	<sup>152</sup> Eu	Bq L <sup>-1</sup>	30 ± 3
Sulfates	g L <sup>-1</sup>	7	<sup>85</sup> Sr	Bq L <sup>-1</sup>	3200 ± 300
Iron	mg L <sup>-1</sup>	400	<sup>90</sup> Sr	Bq L <sup>-1</sup>	350 ± 80
Strontium	mg L <sup>-1</sup>	75.4	<sup>239+240</sup> Pu	Bq L <sup>-1</sup>	1800 ± 300

rated vapor pressures, and values were calculated using the formula:

$$S_{sp} = a_m \cdot N_A \cdot w_m \quad (1)$$

where  $a_m$  – the maximum number of moles of water that is absorbed by 1 g of adsorbent, or monolayer capacity;  $N_A$  – Avogadro's number;  $w_m$  – the area occupied by one molecule of water (1.28 nm<sup>2</sup>).

The efficiency of sorption of cesium was calculated using the distribution coefficient ( $K_d$ ),  $S$ , % – degree of sorption, and  $q_e$  – adsorption capacity, mg/g, which were calculated using the following formulae:

$$K_d = [A_0 - A_p]/A_p(V_L/m_s) \quad (2)$$

$$S = (1 - A_e/A_0) \cdot 100\% \quad (3)$$

$$q_e = K_d A_0 \quad (4)$$

where –  $A_0$  – initial activity, Bq L<sup>-1</sup>,  $A_e$  – equilibrium activity, Bq L<sup>-1</sup>,  $V_L$  – volume of liquid phase, ml,  $m_s$  – mass of the sample of sorbent, g.

### 3 Sorption characteristics of unmodified sorbents and pure ferrocyanides

Data on the sorption of cesium from model solutions simulating LRW are presented in Table 2.

It is known that the distribution coefficient of cesium to unmodified natural sorbents usually does not exceed 100, and is typically two orders of magnitude lower than for ferrocyanide containing sorbents. Among the studied natural sorbents  $K_d$  varied from 17 to 68, with minimum values observed for zeolites, average values for bulk clays, and maximum values for montmorillonite. These data are in good agreement with published data [18, 19].

**Table 2:** Cesium sorption characteristics on (a) unmodified sorbents and pure ferrocyanides, and (b) metal ferrocyanide composites.

(a) Code	S, %	$K_d$
Zeolite	14	17
Red clay	26	35
Yellow clay	21	27
Green clay	26	35
Montmorillonite	40	68
FC Cu	> 98.5	> 5 × 10 <sup>4</sup>
FC Co	89	3.2 × 10 <sup>4</sup>
FC Ni	> 99	> 7.7 × 10 <sup>4</sup>
(b) Code	S, %	$K_d$
Termoksid-35	73	1.1 × 10 <sup>3</sup>
Cu + Z	96	9 × 10 <sup>3</sup>
Cu + RC	> 98	> 3 × 10 <sup>4</sup>
Cu + YC	> 98	> 3 × 10 <sup>4</sup>
Cu + GC	> 99	> 5 × 10 <sup>4</sup>
Cu + MMT	97	1.2 × 10 <sup>4</sup>
Co + Z	50	4 × 10 <sup>2</sup>
Co + RC	55	5 × 10 <sup>2</sup>
Code	S, %	$K_d$
Co + YC	58	5.5 × 10 <sup>2</sup>
Co + GC	58	5.5 × 10 <sup>2</sup>
Co + MMT	56	5 × 10 <sup>2</sup>
Ni + Z	80	1.6 × 10 <sup>3</sup>
Ni + RC	85	2.4 × 10 <sup>3</sup>
Ni + YC	80	1.6 × 10 <sup>3</sup>
Ni + GC	86	2.5 × 10 <sup>3</sup>
Ni + MMT	86	2.5 × 10 <sup>3</sup>

Note: here and further FC – ferrocyanide, RC – red clay, YC – yellow clay, GC – green clay, Z – zeolite, MMT – montmorillonite, composite sorbents codes mean by e.g. Cu+Z – ferrocyanide copper with zeolite etc.

Cesium sorption capacity for the various sorbents decreases in the following sequence: montmorillonite (60.7) > red clay (39.3) > green clay (39.1) > yellow clay > (31.9) > zeolite (21.3) (all values in mg g<sup>-1</sup>). Differences in adsorption capacity reflect the mineralogical and geochemical characteristics of the different sorbents, and are strongly

controlled by specific surface area. Specific surface area varies considerably between the different types of sorbent material (clay materials show a clustering of surface area values between  $659\text{--}775\text{ m}^2\text{ g}^{-1}$ ). Lowest specific surface area was observed for the zeolite ( $365\text{ m}^2\text{ g}^{-1}$ ), and maximum for montmorillonite ( $906\text{ m}^2\text{ g}^{-1}$ ). A close correlation was observed between Cs sorption and specific surface area (Pearson correlation coefficient  $r = 0.92$ ).

This suggests that the basic sorptive mechanism for Cs is physical adsorption, with a certain number of active sites present with high affinity for cesium and which are able to effectively adsorb this radionuclide. The dry metal ferrocyanides showed significantly higher  $K_d$  and adsorption capacity for Cs than the natural sorbents, which is typical of selective sorbents. In this case, best performance was achieved with copper and nickel ferrocyanides, which showed an order of magnitude greater  $K_d$  for cesium, than cobalt ferrocyanide (Table 2a and b). These results are consistent with previous studies [6, 8, 20–22], *e.g.* Sirakanyan *et al.* [14] observed a similar trend for the adsorption of cesium using different ferrocyanides.

## 4 Sorption characteristics of composite materials

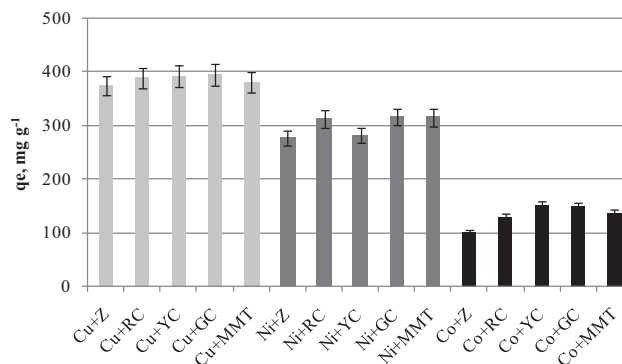
Figure 1 presents data on the sorption of cesium by the metal ferrocyanide composite materials tested, expressed as adsorption capacity. Among the studied composite sorbents the most effective for the adsorption of cesium were those based on copper ferrocyanide. These composites removed 96%–99% of the total content of cesium in solution, with distribution coefficients ( $K_d$ ) ranging from  $9 \times 10^3$  to  $5 \times 10^4$  (Table 2b), and showed adsorption capacities in excess of  $350\text{ mg g}^{-1}$  (Figure 1).

Comparing the different Cu-based ferrocyanide sorbents, those using a clay substrate were the most effective in removing Cs (in terms of adsorption capacity), *i.e.*

$$\begin{aligned} \text{Cu} + \text{GC}(395.1) &> \text{Cu} + \text{YC}(392.5) > \text{Cu} + \text{RC}(388.9) \\ &> \text{Cu} + \text{MMT}(380.8) > \text{Cu} + \text{Z}(374.6) \end{aligned}$$

(all values shown are  $\text{mg g}^{-1}$ )

This trend was not consistently observed when comparing the different metals (*i.e.* Cu, Ni, Co) and absolute differences in adsorption capacity between individual metal ferrocyanides with different mineral substrates were relatively minor, being in the range of 10%–12% and sometimes within experimental error (Figure 1).  $K_d$  values therefore better reflect the specificity of these sorbents.



**Fig. 1:** Sorption of cesium (as adsorption capacity,  $\text{mg g}^{-1}$ ) with different ferrocyanide-based composite materials. See Table 1 for composite sorbent codes.

Among the composite sorbents the most thoroughly studied are materials based on ferrocyanides of nickel [6, 8, 9, 12]. This compound is also used for the synthesis of granulated sorbents – termoxids in which hydrated zirconium or titanium dioxide serves as a mineral carrier. There are several brands of these sorbents (T-3A, T-35, T-55, *etc.*), which are very effective in dynamic sorption. The sorbents produced in the present study by modifying natural materials with nickel ferrocyanide take an intermediate position between the sorption capacity of composites based on copper and those based on cobalt. These composites removed 80%–86% cesium from the model solution, and distribution coefficients are  $(1.5\text{--}2.5) \times 10^3$ . The  $K_d$  values obtained are broadly similar to that obtained using the Termoksid-35 Ni-K ferrocyanide-based commercial adsorbent (Table 2b).

The least effective materials were those based on cobalt ferrocyanide. The  $K_d$ s of the studied Co-based sorbents vary between  $(4\text{--}6) \times 10^2$  (Table 2b), which while remaining an order of magnitude higher than for the unmodified sorbents is significantly lower than for the composites prepared using copper or nickel ferrocyanides.

The data indicate that the properties of the metal used to modify the ferrocyanide, rather than the mineral substrate used, is the most important factor controlling the sorption capacity of the composite. The best sorption properties in relation to cesium were provided by composites based on copper ferrocyanide, and this may be a result of the greater replacement of copper in ion exchange reactions when compared to other metal ferrocyanides [22–24].

To further investigate the kinetics of the sorption processes, and determine the influence of different waste properties (pH, salinity, content of organic complexants) on sorption, the best-performing sorbents were focused

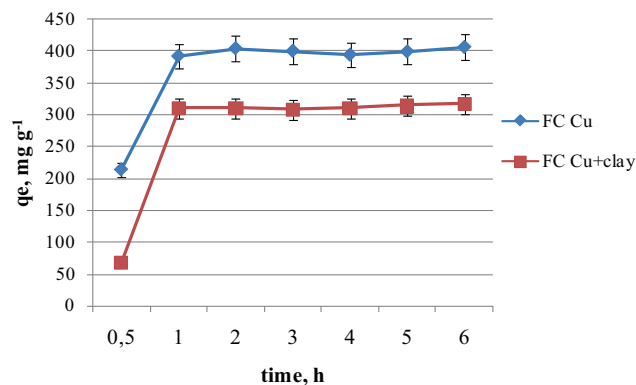


Fig. 2: Kinetics of sorption of cesium on the ferrocyanide sorbents.

on: specifically dry copper ferrocyanides and their composite compounds with clay (in this case, red clay).

## 5 Investigation of the kinetics of sorption of cesium by ferrocyanide sorbents

Kinetic data (Figure 2) show that the selected sorbents reach sorption equilibrium in relation to Cs within 1 h of the beginning of the experiment, indicating relatively rapid adsorption kinetics. The form of the adsorption isotherms corresponds to L-type adsorption (by Langmuir) [26]. Over the remaining 2–6 h of the experiment the adsorption of cesium did not change.

## 6 Effects of different factors (pH, salinity, organic matter) on the extraction of cesium from model solutions of LRW on ferrocyanide sorbents

### 6.1 Effect of pH on the extraction of Cs

Liquid radioactive wastes from NPPs have varying chemical compositions and differing pHs, which are often strongly alkaline. The pH of LRW from reactor BN-350 according to [3] varies between 10 and 12.5. During the processing of LRW and preparation for stages of sorption by various operations (bulk filtration, oxidation of the organic complexing component, *etc.*), the pH can be significantly altered. Cesium is absorbed by ferrocyanides and the composite sorbents across a wide range of pH (Fig-

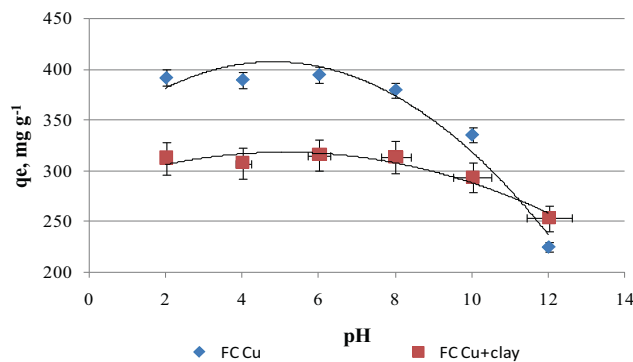


Fig. 3: Effect of pH on the extraction of cesium from the model solution.

ure 3). Dependence of adsorption capacity on waste pH is most closely described by a second-degree polynomial equation (the value of the approximation  $R^2 = 0.92-0.98$ ). At pH values above 10, the adsorption capacity of the composite sorbents and the pure ferrocyanides begins to decline, and for pure ferrocyanide this reduction is more noticeable. Adsorption capacity at pH 12 is decreased by 15%–20% compared to lower pHs. The change of the sorption capacity of the composites is less marked, which may be due to their higher chemical stability in alkaline solutions. However, this needs further validation particularly over the pH range 12–14 for more reliable estimates of the properties of ferrocyanides with and without carriers in highly alkaline solutions. The literature also notes reduction in sorption efficiency due to the enhanced dissolution of metal ferrocyanides in alkaline media [6, 8, 14].

### 6.2 Effect of waste salinity on Cs removal

According to the original data in [3] the salinity of LRW BN-350 is 70–605 g L<sup>-1</sup>. In general, the LRW formed by NPP operations can have a wide range of chemical compositions and salinity. Here, we examine the suitability of the studied composite sorbents for sorption of Cs in different salinities of model solutions. Data on the adsorption of Cs from model solutions with differing salinities are shown in Figure 4.

The data obtained show a decrease in adsorption capacity with increasing salinity in the model solution, as a result of competition effects (as seen in previous studies [8, 20]). However, even at very high salinities (of 500 g L<sup>-1</sup>) sorbents are able to absorb cesium at 200 mg g<sup>-1</sup> and above. Dependence of the change in adsorption capacity on the total salinity is best described by a second-degree polynomial equation (the value of the approximation  $R^2 = 0.95-0.99$ ). The effect of salinity in the

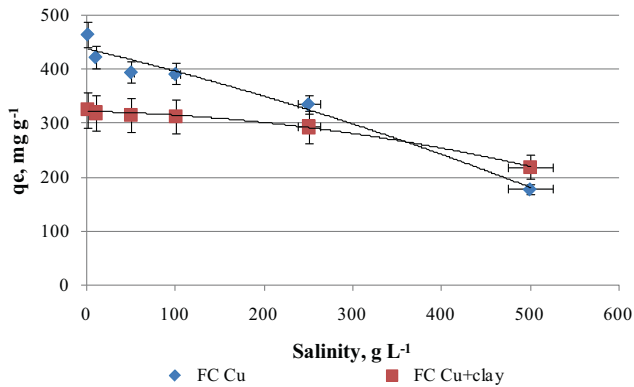


Fig. 4: Effect of salinity on the uptake from the model Cs-bearing solutions.

model solution on cesium extractability is different for the composites and the pure ferrocyanides, *i.e.* the composites are characterized by a gradual reduction in sorption capacity with increasing salinity, whereas for pure ferrocyanide an abrupt reduction in capacity for cesium is observed at salt contents exceeding  $100 \text{ g L}^{-1}$ . At  $500 \text{ g L}^{-1}$  salinity however the composite and the pure ferrocyanide show similar adsorption capacity.

### 6.3 Effect of organic complexing agents on the sorption of cesium by ferrocyanide sorbents

Most of the technologies of LRW treatment include as one of the first stages of waste treatment the destruction of complexants, which greatly reduce the efficiency of selective sorbents [2, 7, 8, 25]. However, not all of the technologies used completely remove the organic matter present. One of the objectives of the present research was to determine the effects of the presence of different concentrations of organic matter, which potentially could remain after oxidation treatment stages. Data for evaluation of the effect of residual complexing agents on sorption by ferrocyanide sorbents from LRW model solutions are shown in Figure 5. The dependence of the change of adsorption capacity on the concentration of organic complexation agents is most closely described by a second-degree polynomial equation (the value of the approximation  $R^2 = 0.97\text{--}0.99$ ). It was noted that carbon contents of  $500 \text{ mg L}^{-1}$  (total organic carbon) barely affected the sorption characteristics of the test sorbents. At higher concentrations however Cs adsorption is significantly reduced, although the composite adsorbent tested (FC Cu + clay) performs significantly better than the pure Cu ferrocyanide, retaining an adsorption

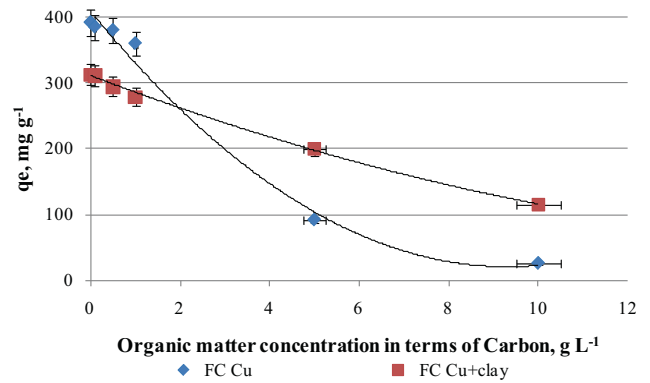


Fig. 5: Effect of concentration of complexing organic matter on the sorption of cesium from model solutions.

capacity of  $>100 \text{ mg g}^{-1}$  even at organic carbon concentrations of  $10 \text{ g L}^{-1}$ . High concentrations of organic complexing agents in solution have been observed to consistently decrease the absorption capacity of cesium by ferrocyanide sorbents by 1.5–2 times [25].

## 7 Conclusion

This article has studied a series of sorbents for their ability to adsorb cesium – the main dose-contributing radionuclide of LRW. Data indicated that the most effective composite materials are copper ferrocyanides applied on bulk mineral sorbents. The distribution coefficients ( $K_d$ ) of Cs on unmodified natural sorbents was *ca.*  $10^2$ , while copper and nickel ferrocyanide composite sorbents showed  $K_d$ s of  $10^3\text{--}10^4$ . The best performing composites were those based on Cu ferrocyanides precipitated onto bentonite clays ( $K_d > 3 \times 10^4$ , adsorption capacity  $395 \text{ mg g}^{-1}$ ), although Cs adsorption capacity is largely independent of the specific mineral substrate used (*i.e.* zeolites, bentonite clays or montmorillonite). Rapid reaction kinetics were observed, with sorption reaching equilibrium within 1 h. Among the factors affecting the extraction of cesium from waste solutions, the most significant effect is from the concentration of organic complexing agents. Cu ferrocyanide on clay still showed effective adsorption of Cs however (adsorption capacity  $>100 \text{ mg g}^{-1}$ ) even at organic contents of  $10 \text{ g C L}^{-1}$ . As they are based on bulk mineral sorbents, these composites provide potentially low-cost materials for effective Cs removal from high salinity LRW. Further work however should test the performance of these composites in real waste solutions, at higher radiation flux.

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