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Coal fly ash as a potential fixation reagent for radioactive wastes

Roy Nir Lieberman^{a,b,*}, Uri Green^a, Giora Segev^{a,c}, Mehmet Polat^d, Yitzhak Mastai^b, Haim Cohen^{a,e,*}

^a Department of Biological Chemistry, Ariel University at Samaria, Ariel 40700, Israel

^b Department of Chemistry and the Institute of Nanotechnology, Bar-Ilan University, Ramat-Gan, Israel

^c Israel Atomic Energy Commission, Tel-Aviv, Israel

^d Department of Chemical Engineering, Izmir Institute of Technology, Turkey

^e Chemistry Department, Ben-Gurion University of the Negev, Beer Sheva, Israel

HIGHLIGHTS

- Fly-ash acts as a blocking barrier for radionuclide cations diffusion.
- Fixation of the radionuclides is via $-AlO_2^-/-SiO_3^-$ anions at the fly ash surface.
- A novel Sr⁹⁰ fixation mode via precipitation and adsorption to the fly ash is found.

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ABSTRACT

Israel produces ~1.3 Mt/year of fly ash (FA), a byproduct of its coal-fired power plants. Due to increasing environmental regulations, these imported coals are processed to reduce the sulfur concentration (~0.6%). These processing methods result in a material that has an enriched alkali/alkali earth component with pozzolanic and basic properties (pH > 10.5).

FAs are utilized worldwide, mainly as a cement additive for the construction industry. Recently, it was demonstrated that Class F FA can act as an excellent fixation reagent for acidic wastes from the phosphate or the oil regeneration industries. In the current work the potential utilization of Class F FAs as fixation reagents for low-activity radioactive waste from the nuclear industry was examined. Aqueous solutions containing radionuclide simulants: cesium (Cs⁺), strontium, (Sr²⁺), and cerium (Ce³⁺, Ce⁴⁺) were used as case studies with promising results. It is suggested that the primary fixation mechanism involves the aluminate/silicate anions at the FA surface. A novel experimental fixation approach utilizing the formation of carbonates is demonstrated and a new interaction mechanism is suggested based on the electrostatic interactions of the positively charged fine precipitates with the negatively charged FA surface.

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1. Introduction

Israel utilizes imported bituminous coal as a primary fossil fuel for power production (>63% in 2013 [1]). Annually, the utilities consume ~13 Mt of coal producing 183,000 tons of bottom ash (BA) and 1.3 Mt of FA [2]. The coals are imported mainly from South Africa but also from Colombia, Australia, Indonesia, and Russia [2] and contain ~10% of inorganic mineral materials.

In line with Israel's strict environmental regulations regarding the emission of pollutants to air via the combustion process [3], the imported coal undergoes beneficiation (via washing with

water) to reduce the organic constituents; primarily sulfur (S) and phosphorous (P) [4] and some trace elements (e.g. Hg, Pb, and As). The result is that the FA produced is rich in alkali and alkali earth elements, pozzolanic with cementitious properties, and is considered to be a Class F FA [2] (which has a basic solution in contact with water). Consequently, when in contact with water, the FA is highly basic, pH > 10.5 at Solid /Liquid ratio of 1/10, due to high lime content (CaO) in the FA. Currently, 100% of the ash (bottom and fly) produced [2] in Israel is utilized in the construction industry either as a cement additive (up to 10% weight content), road structural filler, or other minor applications (e.g. agriculture) [2,5–15]. Thus, its economic value is rather low ≤15 \$/ton.

The possibility of using FA as an effective neutralization and fixation reagent for acidic wastes has been explored and suggested as a more significant economic value added as a utilization method [16–19].

* Corresponding authors at: Department of Biological Chemistry, Ariel University at Samaria, Ariel 40700, Israel. Tel.: +972 54 7776499; fax: +972 8 9200749.

E-mail addresses: roynl@ariel.ac.il (R.N. Lieberman), hcohen@ariel.ac.il (H. Cohen).

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Several mechanisms for the fixation of metal ions and the FA surface have been previously suggested [20–23].

1.1. Cation-exchange

The surface of the FA particles contains several anionic functional groups mainly aluminates $-O-AlO^-$ and silicates $-O-SiO_2^-$: which can behave as a cation-exchange material. Typical metal cations that can undergo fixation to the FA surface are mono- or divalent metal cations (e.g., Cs^+ , Cd^{2+} , Cu^{2+} , and Sr^{2+}).

1.2. Coordinative bonding

Coordinative bonding is formed between the cation and non-bonding electrons of functional groups located at the surface of the FA particles. The cation behaves as a Lewis acid and the FA surface behaves as a Lewis base. This is a mechanism in which the Lewis base donating the lone pair of electrons forms a bond with the metal cation. This interaction is equivalent to the formation of a complex where the surface groups are the ligands. Energetically, it is a relatively strong bond, which can reach a strength of >150 kJ/mol [24]. Typical metal cations that can undergo this interaction are Ce^{III} , Ce^{IV} , or UO_2^{2+} .

The feasibility of this application has also been effectively demonstrated with industrial wastes. The acidic organic waste produced during regeneration processes of used motor oil (via Oleum extraction) yields extremely acidic waste, >10 M H^+ with a high concentration of heavy and toxic metals [17] along with the acidic waste (0.1–1 M) from the phosphate industry (a byproduct of the phosphate rock dissolution process via either sulfuric or hydrochloric acids [16] were both effectively neutralized with a FA fixation method. In both types of wastes (motor oil and phosphate), fixation with FA produces a grey sand-like aggregate. The effectiveness of the toxic and heavy metal content fixation was determined using European Directive [25], the USEPA TCLP 1311 [26], and CALWET [27] leaching procedures. Furthermore, the leaching of trace elements from the scrubbed product is within the Israeli drinking limits criteria [28].

These initial findings demonstrated fixation of acidic and heavy metals in Class F FAs and therefore have the potential ability to reduce the costs of low activity radioactive wastes treatment produced in the nuclear energy industry.

Unlike other industrial wastes, the hazard level of all nuclear waste – its radioactivity – diminishes with time. Each radionuclide contained in the waste has a half-life – the time taken for half of its atoms to decay, and, thus for it to lose half of its radioactivity (assuming that the product of decay are not radioactive by themselves). The half-life of radionuclides can vary from seconds to millions of years (see below). Radionuclides with long half-lives tend to be alpha and beta emitters – making their handling easier – while those with short half-lives tend to emit the more penetrating gamma rays. Eventually all radioactive wastes decay into non-radioactive elements. The more radioactive an isotope is, the faster it decays.

The main objective in managing and disposing of radioactive (or other) waste is to protect people and the environment. This means isolating or diluting the waste so that the rate or concentration of any radionuclides returned to the biosphere is harmless. To achieve this, practically all wastes are contained and managed – some clearly need deep and permanent burial. From nuclear power generation, none is allowed to cause harmful pollution. High-level wastes, which contain 19% of the total activity of accumulated liquid radioactive wastes, are the most dangerous. The activity of high-level wastes is determined by the high concentrations of isotopes ^{137}Cs , ^{134}Cs , and ^{90}Sr , as well as by the presence of long-lived actinides. The ecological risk due to intermediate-level wastes is

associated with the fact that the activity of these wastes comprises the main fraction of the total activity of all accumulated liquid radioactive wastes. [29].

FA has demonstrated fixation properties and has the potential to reduce storage and treatment costs of various wastes. It can also potentially service the nuclear industry by partially substituting other storage materials (concrete, bitumen), which are currently utilized. The current work focuses on the ability of the FA to fixate the following types of radionuclides occurring in typical radioactive wastes [30–34]:

- (i) Cs^{137} is one of the main nuclear fission byproducts of U^{235} in nuclear power plants (with a half-life of 30.17 years [31]). This radionuclide decays via emission of β rays (0.19 MeV) to form metastable nucleus of Barium (^{137m}Ba) – Ba^{137m} , which further decays relatively fast (2.6 min) via emission of γ rays (0.60 MeV) to the stable isotope of Barium Ba^{137} .
- (ii) Sr^{90} This radionuclide is also one of the major nuclear fission byproducts of U^{235} . Its half-life is 28.90 years [30] and it decays via β irradiation emission (0.546 MeV) to a stable isotope of Yttrium Y^{90} .

These two radionuclides have a medium half-life and have to be stored for centuries until decaying to a low-level background radiation.

- (iii) **Actinides** The Actinides, which are one of the main byproducts during fission, are all radioactive. They are usually formed via neutron capture by U isotopes (mainly U^{238}) and have relatively very long half-lives. These actinides are f-block elements, filling the 5f electron shell and are also α emitters. Typical actinides are the plutonium – **Pu** or Americium – **Am** [35].

2. Experimental

2.1. Fly ash characterization

The FA used in the current study is the combustion waste product from South African (SA) and Colombian (CO) coals used in Israel and were supplied by the Israeli Electricity Company. In this paper, the two FA types will hereby be referred to (adding a SA or CO prefix) as SAFA or COFA. The SA and CO coals after beneficiation contain 13.9 wt.% and 8.7 wt.% ash and have a spatial density of 0.98 g/cm³ and 0.85 g/cm³, respectively. The ambient air quality standards used in Israel require a low content of S and P in the combustion process. The FA product of these pretreated coals leads to the enrichment of the ash with alkali and alkali earth elements, mainly Ca. The FA particles [11,36] are spherical and have a diameter of between 3 and 250 μm (Fig. 1). Moreover, XRD analysis was performed on both the SAFA and the COFA (Fig. S1).

The FA mainly contains two different types of spherical particles. Cenospheres (Fig. 1C) are hollow “glass bubbles” [37] of aluminosilicates. These particles also contain carbon dioxide or nitrogen which give the ash lightweight properties [37–39]. The second type are the Pleurospheres [40] (Fig. 1D) which are “hollow glass bubbles” filled with smaller glassy particles. In addition, some minerals such as spinels are also present within the FA [41]. FA particles have a relatively large surface area for a non-porous material [2] (1.05 ± 0.1 m²/g for SAFA and COFA). The averaged chemical analysis of both the SAFA and COFA is presented in Table 1.

EDAX analysis of the FA surface functionality presented in Fig. 1 show that SAFA and COFA have similar concentrations (surface coverage) of Si and Al.

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