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ORIGINAL PAPER

Investigating the chemical stabilization of hazardous waste material (fly ash) encapsulated in Portland cement

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Abstract Portland cement has been suggested as an effective stabilization (physico-chemical) method for hazardous waste. This research explored the immobilization of metals in various mixtures of Portland cement and fly ash waste sampled from coal power plant in the province of Lodz, central Poland. The stabilization of fly ash in Portland cement was investigated under a wide range of pH conditions (3–12). Leachability tests were used to determine the efficiency of the encapsulation by studying the dissolution of alkaline metals (sodium, potassium) and alkaline earth metals (calcium, magnesium). The lowest value of leached metals was obtained for ratio of ash to cement of 1:10 in a case of sodium and calcium, while ratio 1.5 gave the lowest leached effects for potassium and magnesium. The high effectiveness of solidification/stabilization process was gained in high pH values (9–11).

Keywords Electrical power plant waste · Coal · Leaching · Physico-chemical waste utilization

Introduction

Solidification/stabilization (S/S) is one of the physical–chemical pre-landfill treatment processes that can be used for fly ash, which requires a special utilization as the hazardous waste listed in the European Catalogue on Hazardous Waste (EPA, Environmental Protection Agency 2002) with the code 10.01.02. The fly ash originates from coal as the inorganic thermal waste from power station and it is estimated in millions tons per year which is significant for environment. The coal deposits often contain impurities such as radioactive elements in ores which can be also found in fly ash after the combustion process (Zielinski and Finkelman 1997).

The solidification/stabilization (S/S) process can be used to encapsulate the wastes by adsorption (Wu et al. 2012; Wang et al. 2009), hydration (Poon et al. 2003) or precipitation reactions with cement and water (Gitari et al. 2010). The results of these interactions are the stabled forms of waste which are non-hazardous or less hazardous than raw material (Zheng et al. 2010; Maschio et al. 2011; Colangelo et al. 2012). It is important to optimize the S/S process parameters to have adequate resistance of the end products to aggressive agents that can appear in the environment i.e. acid groundwater or rainfall (Pandey and Singh 2010). Before the landfill, which is the most popular constituent of waste storage, the environmental characterization is required on crushed mortar samples according to the European standard procedure including in Council Decision 2003/33/EC (2003). The pH dependence test is the best to characterize the general leaching behaviour of elements in cement-based products and it is a tool in a creation of different exposure scenarios (Aubert et al. 2007; Cetin et al. 2012).

Various pH of a soil structure that influences the natural biodiversity has its origin in leachability of collected waste. Monitoring of the end product behaviour in different pH solutions allows optimizing its storage condition. Decreasing percolation of the contaminants from the final products can be also achieved by the establishment of the proper proportion of binder and immobilized waste (Liang et al. 2008). According to the Council Decision 2003/33/EC (2003), establishing criteria and procedures for the acceptance of waste at landfill pursuant, most of the

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scientific interests focus on the heavy metals (Dermatas and Meng 2003; Shim et al. 2005). Nevertheless, the results obtained for alkaline metals and alkaline earth metals like Na, K, Ca and Mg create a significant part of the completed risk assessment scenario. The participation of these metals in the waste and binder mixture decides about the final chemical properties of the products as well as the stabilization of utilized waste.

The scope of the study was to investigate the final product stabilization consisting of the Portland cement and fly ash sampled from the electrical power plant, Belchatov, Lodz Province, Poland. The aim was realized by the fly ash/cement ratio optimization to create the most stable product, as well as finding the correlation to the immobilization of chosen alkaline metals and alkaline earth metals in various pH solutions.

Materials and methods

Experiments

The Municipal solid waste incinerator fly ash (FA), which came from the electrical power plant Belchatov was used in the experiments. A regular portland cement (PC) I 42.5 R of Cement Lafarge S.A. Poland was used as the binder.

The mortar samples $2 \times 2 \times 1.5$ cm^3 were prepared for analysis. The water/mortar ratio was 0.5. The samples were cured for 72 h at 25 °C.

Five series (A–E) of the samples were prepared and subjected to identical exposure and testing. The stabilized waste contained different loadings of fly ash: 10 wt%, 20 wt%, 40 wt%, 50 wt% and 60 wt%. These correspond to the fly ash/cement ratio: A—0.1; B—0.25; C—0.67; D—1.00; E—1.50.

Metal leachability measurements of the raw materials and stabilized ash forms after 48-h exposure were carried out according to European Standard method 12457-2 (2002). All the leaching tests were carried out on the samples in duplicate.

Analysis

Fly ash composition

The metal composition of the fly ash was determined by atomic absorption spectrometry using spectrometer GBC 932 Plus (air–acetylene flame) following the European Standard 12457 (2002). The EA 1108 CHNS—O Analyzer Fisons Instrument equipped with autosampler AS 128, GC column SS PQS (2 m) and thermal conductive detector (TCD) was used to measure carbon, hydrogen and sulphur in the fly ash.

Leachability tests

Metal concentrations of water extracts at different pH solutions (3–12) were measured by atomic absorption spectrometer GBC 932 Plus (air–acetylene flame) according to the CEN/TS European Standard 14429 (2005). The results were presented in milligrams per kilogram of sample dry mass (mg/kg d.m.).

XRD analysis

The XRD studies were carried out on powdered samples. The analysis was conducted using a PANanalytical Model X'Pert PRO MPD using Cu Kα radiation source in the 2θ range from 5° to 90° at 40 kV and current 40 mA. The crystalline phases were identified according the International Centre of Diffraction Data—PDF—2.

Data analysis

The effect of chosen metal leachability in stabilized samples of various ratio fly ash/cement in different pH was investigated using a one-way ANOVA analysis with StatistiXL Version 1.8.

Results and discussion

The chemical analyses results of the fly ash (Table 1) showed that silica, calcium and aluminium were the primary constituents found in the waste samples under investigation. These results were confirmed by XRD analysis shown in Fig. 1. These three constituents in oxide form made up approximately 72 % of the total mass of the fly ash composition.

Table 2 shows the potential maximum leachability for studied material. The analysis of the starting materials of fly ash and Portland cement (before encapsulation/mixing) allowed the maximum potential leachability of the studied metals (Na^+, K^+, Ca^{2+} and Mg^{2+}) to be investigated. The calculations were based on the analyses of leachability of each of the investigated metals in powder samples for FA and PC.

As shown in Table 2 for three of the investigated elements (Na^+, K^+, Ca^{2+}), the potential leachability of the starting materials was directly proportional to fly ash addition, while Mg^{2+} was inversely proportional.

The appropriate choice of binders can decrease the permeability of stabilized waste forms, in which pollutants are physically isolated from aggressive agents (Rendell and Jauberthie 1999). One of the interactions of contaminants with environment and binder is pH-dependent precipitation which involves a fixation mechanism in products (Glasser

1997; Wang et al. 2006). In Fig. 2, the chemical stabilization of alkaline metals (Na^+, K^+) and alkaline earth metals (Ca^{2+}, Mg^{2+}) are given for cement-bound matrices as the function of pH. The results were observed for stabilized waste with different fly ash loading: 10 wt% (A), 20 wt% (B), 40 wt% (C), 50 wt% (D) and 60 wt% (E).

In a case of Na^+, no significant differences were observed between the mixture ratio of cement and fly ash (p value <0.05). The leachability increased at a pH of 11 and reaches its maximum at a pH 12. Such the results were observed for all the analyzed samples. For K^+, the lowest concentration of this metal were observed in the samples which consisted of 60 wt% of fly ash and 40 wt% of cement (E) while the highest leachability was in the samples with the lowest loading of fly ash (A). The pH changes did not influence significantly the leachability of K^+. Nevertheless, some significant differences in the leachability were observed (p value 0.98) between the different sample series (A–B). The lowest concentration of Ca^{2+} was observed after leachability test investigations in the stabilized forms included only 10 wt% of fly ash (A). For all the samples, the significant regression was observed at a pH 10 and almost no metal leached was obtained at a pH 12. No significant results of leachability were obtained between the different loadings of fly ash/cement samples in the investigated sample series (p value <0.05). Analyses of Mg leachability gave the lowest concentration of this metal in the samples of 60 wt% loading of fly (A), while the

Table 1 Chemical composition of fly ash (FA) and Portland Cement I 42.5 R (PC)

Oxide	FA (wt%)	PC (wt%)
SiO_2	42.97	18.9
Al_2O_3	16.96	5.3
CaO	11.85	62.7
Fe_2O_3	4.97	2.7
K_2O	4.21	
Na_2O	3.80	0.73
SO_3	3.61	3.13
TiO_2	0.99	
MgO	0.83	1.5
P_2O_5	0.13	
MnO_2	0.02	

Table 2 Potential leachability of chosen metals in studied material [mg/kg d.m.]

	Ratio = FA/PC	Na	K	Ca	Mg
PC	0/100	487.50	970.52	663.60	22.00
FA	100/0	1,828.35	984.70	874.27	1.30
PCFA	100/100	2,315.85	1,955.22	789.60	22.11
PC	A 0.1	438.75	873.47	597.24	19.80
FA		182.83	98.47	87.43	0.13
PCFA		621.58	971.94	684.67	19.93
PC	B 0.25	390.00	776.42	530.88	17.60
FA		365.67	196.94	174.85	0.26
PCFA		755.67	973.36	705.73	17.86
PC	C 0.67	292.5	582.31	398.16	13.20
FA		731.34	393.88	349.71	0.52
C		1,023.84	976.19	747.87	13.72
PC	D 1.00	243.75	485.26	331.80	11.00
FA		914.17	492.35	437.13	0.65
PCFA		1,157.92	977.61	768.93	11.65
PC	E 1.50	195.00	388.21	265.44	8.80
FA		1,097.01	590.82	524.56	0.78
PCFA		1292.01	979.03	790.01	9.58

PC cement, *FA* fly ash, *PCFA* mixture of cement and fly ash

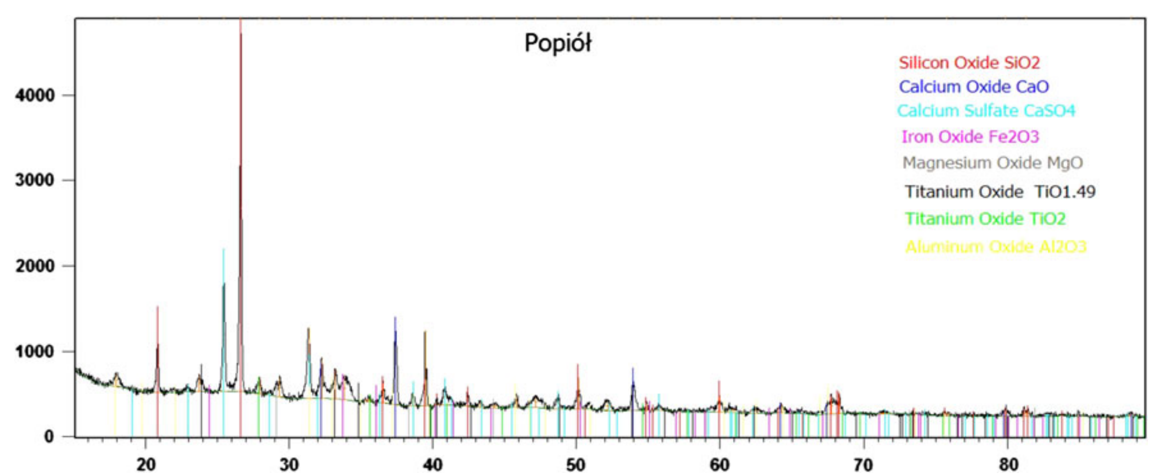

Fig. 1 XRD analysis of fly ash sample

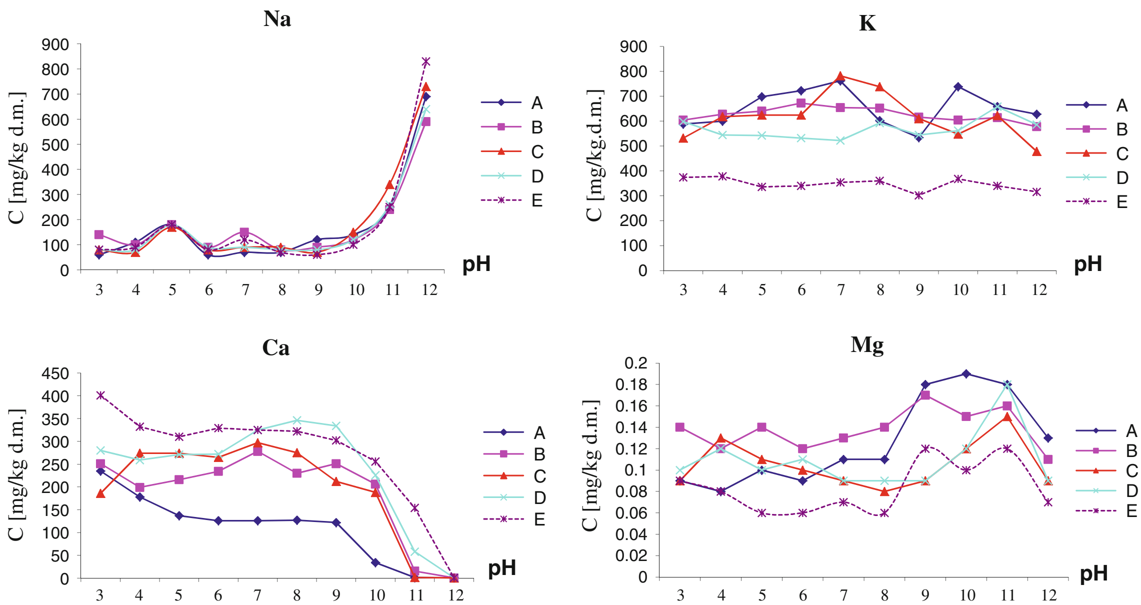

Fig. 2 pH influence on the leachability of chosen metals from different loading FA and PC samples

highest concentration of Mg^{2+} was observed in the 10 wt% loading. For all the samples, pH values in a range of 3–8 do not influence the leachability of Mg^{2+}. In strong alkaline solution the leachability of Mg^{2+} increased for all the analyzed samples. The various sample series ratio of fly ash/cement did not influence significantly the leachability of this metal, p value <0.05.

The surface adsorption of metal ions on the stabilized forms of fly ash and cement, as well as the presence of salt forms and dissociated ions in the solution were pH dependent. Some formation of metal complexes and precipitation of metal salts occurred as the ultimate result of pH changes (Valls and Vazquez 2000; Galiano et al. 2010; Batchelor 2006).

The aqueous phase presented in the pore structure of cement-based waste forms was alkaline which influenced the precipitation of insoluble compounds (Li et al. 2001; Glasser and Zhang 2001). The amount of hydrated phases did not influence on the high pH of pore fluids (Glasser 1993) and this effect was a result of continued retention of metallic contaminants in a waste form.

The leachability of alkaline and alkaline earth metal ions from the stabilized waste forms and the adsorption into the nanoporous of these forms surfaces influenced the calcium silicate hydrate (C–S–H) gels. The C–S–H gels have been known as the naturally existed geological forms characterized of a high persistence for a long time (Tiruta-Barna et al. 2004). These gels have been a part of cement chemistry and were created during the solidification process. Their properties were directly depended on the mortar composition (Hong and Glasser 1999). The surface charge of C–S–H has been about zero when the calcium silicon (Ca/Si) ratio was about 1.2 (Maschio et al. 2011; Glasser 1993).

Based on the fly ash and cement composition Table 1, the Ca/Si ratio was calculated in different mortar samples that corresponded to the different fly ash loading: 10 wt% (A), 20 wt% (B), 40 wt% (C), 50 wt% (D) and 60 wt% (E). According to the waste included in the samples, the Ca/Si ratio were: A—2.7, B—2.2, C—1.5, D—1.2 and E—1.0. For these calculations, the neutral charge of the C–S–H gel was expected for the samples with the 50 wt% loading of fly ash (D). In the samples A, B and C where the calcium dominated C–S–H gel had a positive surface charge and anions may occur while silicon-rich C–S–H gel (samples E) adsorbed cations. Nevertheless, the obtained results generally divided the analyzed metals for two groups. To the first one belonged Na and Ca, where the high concentration of these metals was observed in the fly ash loading of 60 wt% (E). To the second group, K and Mg belonged and high amount of the fly ash in the mortar sample (E) decreased these metals' concentration in the solution.

The properties of the S/S waste especially near surface area depended on the aggressive reagents' attack including pH changes and caused the degradation of stabilized waste forms. Chemical immobilization of pollutants in S/S process depended also on the crystalline phase of binder matrix (Zheng et al. 2010). Portland cement used in the study contained about 1 wt% of Na_2O and K_2O, which afforded the high hydroxide ions concentration in pH 12 and suppressed the calcium solubility. Portlandite which dominated in the PC composition buffered the surface pore solution during the alkali metals leaching. It minimized the chemical interactions between the contaminants and

Table 3 Immobilization of analyzed metals at different pHs [%]

Metal	Sample	pH									
		3	4	5	6	7	8	9	10	11	12
Na	A	78.37	82.43	68.78	85.82	74.43	87.72	87.06	78.80	61.57	2.08
	B	91.16	81.27	75.61	90.78	90.21	91.49	81.59	77.13	65.56	3.40
	C	89.91	90.51	79.00	90.51	88.53	88.73	91.50	83.24	59.24	12.75
	D	91.17	92.21	80.91	91.00	90.55	91.56	92.09	87.40	72.20	33.26
	E	92.27	91.85	83.30	92.28	87.85	93.43	94.50	89.55	78.33	15.14
K	A	41.90	32.57	22.59	27.24	16.93	40.92	50.89	16.62	32.62	33.35
	B	31.62	28.08	42.98	36.54	43.32	44.12	35.20	28.74	29.63	36.31
	C	20.09	10.72	17.06	16.36	12.58	14.37	21.59	29.21	22.80	27.55
	D	30.41	28.73	21.63	26.12	2.77	7.82	51.99	31.85	21.24	40.96
	E	52.31	54.81	58.86	56.68	52.71	55.43	63.47	49.27	61.10	57.36
Ca	A	67.04	71.60	78.43	81.98	80.50	82.31	84.07	94.52	99.82	99.88
	B	70.66	50.04	60.24	56.40	55.52	64.20	65.17	67.12	99.79	99.92
	C	56.66	63.07	63.46	61.98	51.50	60.57	58.30	68.49	97.46	99.91
	D	53.44	62.03	56.73	59.06	48.63	41.88	50.28	64.27	90.63	99.91
	E	36.64	50.81	52.97	48.05	46.20	50.59	54.73	56.26	78.17	99.90
Mg	A	99.57	99.56	99.46	99.56	99.42	99.47	99.19	98.95	99.10	99.33
	B	99.44	99.42	99.66	99.61	99.59	99.69	99.22	99.31	99.30	99.59
	C	99.15	98.69	98.99	99.11	99.14	99.25	99.18	99.00	98.66	99.20
	D	98.90	98.84	98.95	98.91	99.06	99.06	99.12	98.75	98.09	99.07
	E	98.18	98.53	98.25	98.44	98.23	98.23	97.90	97.89	98.13	98.48

surface of the stabilized waste (Shi and Fernandez-Jimenez 2006). This effect was observed for both of the alkali earth metals whose solubility significantly decreased in the highest value of pH solution.

Table 3 has compiled the percentage yield of solidification process of FA and PC as the binder. The analyzed samples with various loading of FA (A–E) were processed by different pH solutions to estimate the durability of metals' immobilization in stabled waste forms. In a case of alkali metals, the best results of encapsulation were obtained for the samples with 60 wt% loading of FA (E) in pH 9, while the most effective adsorption for alkali earth metals was obtained in pH 12 for the samples with 20 wt% loading of FA. Nevertheless, the high values of solidification for Ca^{2+} and Mg^{2+} in the samples with 60 wt% loading of FA were also observed. Most of the Table 3 results maintained the high yield of immobilization effects in the alkaline solutions, which should be taken for the further consideration of the stabilized waste risk assessment scenario in environment.

Fly ashes and their disposal has been a current issue affecting the global environment (Iyer and Scott 2001) including Lodz Province, which is an important agglomeration in central Poland with a population of 2.6 million inhabitants. In 2009, 13,732.4 tons of wastes were created in this region where 5,074.8 tons came from the thermal processes of power plants (PIEP, Provincial Inspectorate for Environmental Protection of Lodz 2010).

Exposure to the environment has had significant effects on waste chemical landfill storage and the acidity was one of the parameters deciding this (Otero-Rey et al. 2005). It has been important to monitor the pH of the landfill wastes and optimize the process parameters to slow the chemical reactions between the environment and immobilized pollutants.

Conclusion

The fly ash waste management has been an important issue in the worldwide environment therefore, their proper collection and disposal have been important as they can directly impact the health risks.

Landfilling as the most popular form of waste disposal in Central and Eastern Europe should focus on the effectiveness of solidification and stabilization (S/S) processes of the wastes before their storage.

The proper composition of the waste mixture and a binder should be held in the planning of S/S process to obtain the most stable forms of the immobilized contaminants. In the experiments made under this work, the stabilization effects were characterized by the leachability tests. The lowest concentrations for the analyzed metals in the solutions were obtained for 10 wt% loading of fly ash (FA) samples in a case of Na^{+} and Ca^{2+}, while the 60 wt% loading of FA samples gave the low leached effects for K^{+} and Mg^{2+}.

The low changes of the pH range should be provided during the storage process of the stable wastes to limit the leachability of the pollutants to the environment. For alkaline and alkaline earth metals studied under this work, the high value of pH (9–11) should be retained to give the most effective yield of S/S process.

With the results obtained in these studies the most optimized composition of the FA/PC mortar should consist of FA 60 wt% loading and landfill storage of the stabilized waste should not exceed the pH range of 9–11 to hold the most effective encapsulation of contaminants.

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