

Thermal Conversion of Heavy Metal Chlorides (PbCl₂, CdCl₂) and Alkaline Chlorides (NaCl, KCl) into Phosphate Glasses

Sébastien Donze, Lionel Montagne,* and Gérard Palavit

Laboratoire de Cristallochimie et Physicochimie du Solide-UPRESA CNRS 8012,
Ecole Nationale Supérieure de Chimie de Lille, BP 107 59652 Villeneuve d'Ascq, France

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Fly ashes resulting from municipal solid waste incineration contain lead and cadmium chlorides (PbCl₂, CdCl₂) that volatilize during the thermal treatment and vitrification. They are recovered in "secondary ashes". We report the thermal conversion of lead and cadmium chlorides into phosphate glasses, using ammonium dihydrogen phosphate (NH₄H₂PO₄) as a precursor. Two synthetic batches containing (PbCl₂ + CdCl₂), and (PbCl₂ + CdCl₂ + NaCl + KCl) were mixed with NH₄H₂PO₄ in variable amounts. The (NaCl + KCl)/(PbCl₂ + CdCl₂) ratio in the batches to be converted was chosen to reflect the secondary ash composition. The resulting glasses contain 20–60 mol % P₂O₅. Elemental analyses of the glasses are compared with the calculated data from two conversion reaction models. The first one involves the reaction of NH₄H₂PO₄ with chlorides only, the second addition involves a high-temperature conversion reaction of chlorides with water. The second mechanism is in good accordance with the experimental results for PbCl₂ + CdCl₂ mixtures. In the case of PbCl₂ + CdCl₂ + NaCl + KCl mixtures, the conversion of lead and cadmium chlorides into phosphates is optimum for glasses containing more than 45 mol % P₂O₅.

Introduction

The residues from municipal solid waste (MSW) incineration, mainly bottom ashes and fly ashes, contain considerable amounts of toxic heavy metal (Pb, Cd, Zn, Hg) salts and have to be deposited into a waste dump for hazardous materials. These products have to be stabilized before storage. Vitrification processes, i.e., electric arc melting,^{1–3} plasma melting,^{4–7} or cyclone furnace process,⁸ are developed in order to ensure the confining of polluting elements in a glassy or crystallized matrix. However, a fraction of heavy metals volatilizes during the fly ash vitrification process and have to be captured. The installation of a dry quench at the furnace outlet to filter these heavy metals leads to the recovery of polluting elements as chlorinated salts, called secondary ashes.⁹ The thermal treatment of the secondary ashes must involve, in a first step, the conversion of the toxic chlorinated salts into a thermally stable form. After such a treatment, the secondary ashes can be vitrified to produce a glass matrix, which ensures a complete encapsulation of the pollutants.¹⁰

Most of the processes of chlorinated heavy metal conversion entail the precipitation of the polluting elements in a basic medium.¹¹ Heavy metals are recovered as hydroxides; however, such processes imply the treatment of high volumes of solutions by appropriate processes. Ikeda et al.¹² have studied the thermal conversion reactions of metal chlorides into oxides with boric acid to develop a method for the vitrification of radioactive molten salt wastes. Since it avoids the treatment of large volumes of solution, such a solid state thermal process appears to be interesting for the conversion of heavy metal chlorides. However, the conversion reaction with boric acid occurs at 1000 °C, which is higher than the volatilization temperature of chlorinated heavy metal salts such as PbCl₂ (950 °C) and CdCl₂ (960 °C).

It has been reported¹³ that stannous chloride (SnCl₂) reacts with ammonium dihydrogen phosphate (NH₄H₂PO₄) to produce phosphate glasses of the SnO–SnCl₂–P₂O₅ system. During glass preparation and depending on compositions, the chlorine atoms are replaced more or less by oxygen atoms. We propose to convert into oxide the lead and cadmium chlorides generated during the fly ashes vitrification processes, through a reaction with phosphates. This paper reports the solid state thermal conversion of heavy metal chlorides MCl₂ (M = Pb, Cd) into oxides, with ammonium dihydrogen

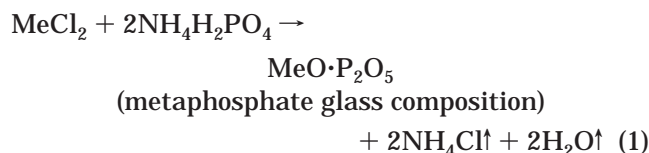
* Corresponding author. E-mail: lionel.montagne@univ-lille1.fr.

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phosphate as a glass precursor. Lead and cadmium salts are chosen because they are among the most volatile ones present in the secondary ashes.¹⁴ Since iron phosphate glasses are proposed as host materials for the encapsulation of high level nuclear wastes,^{15,16} a thermal process which leads to the formation of phosphate glasses is a promising way for the conversion and stabilization of heavy metals into a durable glass matrix.

The conversion reaction can be described as follows:



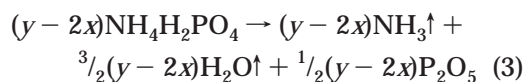
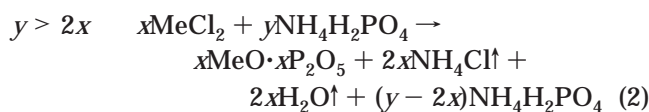
The use of $\text{NH}_4\text{H}_2\text{PO}_4$ as a phosphate precursor leads to the recovery of chlorides under a solid form, ammonium chloride (NH_4Cl), a white powder which sublimates from 250 °C. This enables easy removal of this chlorinated byproduct from the reactor.

The amount of heavy metal chlorides converted and the nature of the resulting phosphate glass depend on the batch composition (the written equations only correspond to the reaction mechanism):

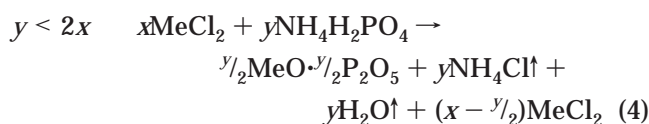
for a stoichiometric batch composition

reaction 1

with $\text{NH}_4\text{H}_2\text{PO}_4$ in excess



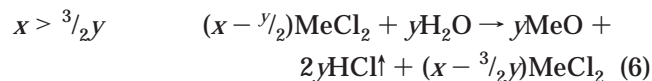
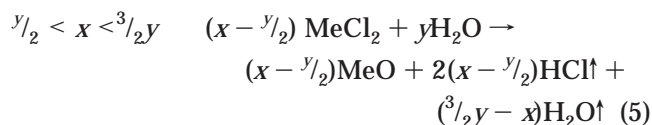
with MeCl_2 in excess



In the following text, this conversion mechanism will be called the *phosphate conversion model*. According to this model, we can observe that the chloride conversion is predicted to be complete only if $y \geq 2x$ (reactions 1 and 2).

We can also notice that water formation occurs during this conversion reaction due to the thermal degradation of $\text{NH}_4\text{H}_2\text{PO}_4$. Jakob et al.¹⁷ have modeled the influence of chlorides on the cadmium evaporation and reported that the presence of water limits the heavy metal volatilization. So, we propose a second model, called the *phosphate and water conversion model*. In this model, it is considered that residual metal chlorides

(in the case $y < 2x$, reaction 4) react with the water generated during the process and are then incorporated as oxides into the phosphate matrix (reactions 5 and 6).



Elemental analyses were performed to determine whether the conversion mechanism of these heavy metal chlorides occurs according to the phosphate or the phosphate and water conversion model.

First, we have studied the conversion of a synthetic mixture containing only PbCl_2 and CdCl_2 . Then, to estimate the efficiency and the applicability of the conversion mechanism proposed for the treatment of secondary ashes, mainly composed of alkaline chlorinated salts,¹⁰ we have studied the influence of the alkaline chlorides (NaCl , KCl) on the lead and cadmium chloride conversion.

Experimental Section

Two groups of synthetic chloride mixtures were prepared. The first contained only PbCl_2 and CdCl_2 (samples A–G). In the second, we have added NaCl and KCl (samples labeled x -700 and x -900 ($x = 1$ –6)). CdCl_2 was prepared by melting $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ for 2 h at 650 °C. The quantities of the respective chlorides were chosen to correspond to the relative contents in the secondary ashes, generated during the vitrification process of fly ashes.¹⁰ Tables 1 and 2 show the nominal compositions of the different batches as weighed. The Pb/Cd atomic ratio chosen for all batches was 4.

The heating rate was 10 °C/min with intermediate 1 h holds at 200, 300, and 400 °C. NH_4Cl was recovered as a white powder by condensation at the furnace outlet during these holds.

Batches A–G were melted at 900 °C for 2 h. For samples x -700 and x -900, the melting temperature and melting hold time were 700 °C and 900 °C, for 30 min and 2h, respectively. Phosphate glasses were obtained by quenching the melts on a brass plate.

Analyzed phosphate glass compositions are listed in Tables 1 and 2. For elemental analyses 0.25 g of the glass samples was completely dissolved in 100 mL of distilled water and 2 mL of HNO_3 (68%). The heavy metal content in the glasses was determined using a Perkin-Elmer 2380 atomic absorption spectrometer. Chlorine was analyzed by potentiometric titration. P_2O_5 content was measured colorimetrically with the yellow vanado–molybdate complex. Sodium and potassium concentrations were determined using a Jenway PFP 7 emission flame photometer.

Results

$\text{PbCl}_2 + \text{CdCl}_2 + \text{NH}_4\text{H}_2\text{PO}_4$ Mixtures. Figure 1 shows the analyzed amounts of Pb, Cd, and Cl versus the P_2O_5 content in the lead–cadmium–phosphate glasses, compared with those calculated with the phosphate conversion model. It appears that experimental data for Pb and Cd are in good agreement with the results predicted by the model, for P_2O_5 contents ranging from 20 to 60 mol %. Experimental chlorine contents are fitted by the phosphate conversion model for phosphate glasses that contain more than 50 mol % P_2O_5

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Table 1. Batch Composition of Lead and Cadmium Chloride Mixtures Converted with $\text{NH}_4\text{H}_2\text{PO}_4$ at 900 °C and Formulation of the Phosphate Glasses

batch composition (g)				glass composition (atom %) ^a				
PbCl ₂	CdCl ₂	NH ₄ H ₂ PO ₄	sample	Pb	Cd	Cl	P	O
9.28	1.53	2.40	A ^b	18.5 ± 0.3	4.4 ± 0.05	21.2 ± 0.5	12.5 ± 0.3	43.5
8.84	1.46	3.05	B ^b	16.1 ± 0.3	3.9 ± 0.05	13.5 ± 0.5	15.2 ± 0.3	51.3
8.39	1.38	3.72	C ^b	14.5 ± 0.3	3.7 ± 0.05	6.2 ± 0.5	17.3 ± 0.3	58.3
8.08	1.06	6.65	D	13.8 ± 0.3	3.6 ± 0.05	3.4 ± 0.5	18.2 ± 0.3	61.1
7.44	1.23	5.13	E	11.2 ± 0.3	2.9 ± 0.05	0.3 ± 0.5	20.5 ± 0.3	65.2
6.43	1.06	6.65	F	8.5 ± 0.3	2.0 ± 0.05	0.1 ± 0.5	22.6 ± 0.3	66.9
5.33	0.88	8.27	G	6.3 ± 0.3	1.6 ± 0.05	0.1 ± 0.5	24.0 ± 0.3	68.0

^a The elemental analyses were performed for all elements except for oxygen. The oxygen content is calculated on the basis of charge balance. ^b Devitrified samples.

Table 2. Batch Composition of Sodium, Potassium, Lead, and Cadmium Chloride Mixtures Converted with $\text{NH}_4\text{H}_2\text{PO}_4$ and Formulation of the Phosphate Glasses Obtained at 700 °C and 900 °C

samples	batch composition (g)					NH ₄ H ₂ PO ₄
	NaCl	KCl	PbCl ₂	CdCl ₂		
1	2.328	2.970	2.216	0.365		3.818
2	2.136	2.725	2.033	0.335		4.505
3	2.012	2.567	1.915	0.316		4.949
4	1.772	2.260	1.686	0.278		5.811
5	1.598	2.038	1.521	0.251		6.825
6	1.430	1.824	1.361	0.224		7.417

samples	glass composition (atom %) ^a						
	Na	K	Pb	Cd	Cl	P	O
	Melting Temperature 700 °C						
1-700 ^b	15.4 ± 0.5	13.2 ± 0.5	2.6 ± 0.05	0.7 ± 0.01	20.1 ± 0.5	11.6 ± 0.3	36.6
2-700 ^b	13.4 ± 0.5	12.1 ± 0.5	2.5 ± 0.05	0.6 ± 0.01	15.7 ± 0.5	13.7 ± 0.3	42.1
3-700 ^b	12.3 ± 0.5	11.2 ± 0.5	2.3 ± 0.05	0.6 ± 0.01	12.6 ± 0.5	15.1 ± 0.3	46.1
4-700	10.7 ± 0.5	9.8 ± 0.5	2.0 ± 0.05	0.5 ± 0.01	6.1 ± 0.5	17.5 ± 0.3	53.4
5-700	9.4 ± 0.5	7.5 ± 0.5	1.8 ± 0.05	0.5 ± 0.01	2.7 ± 0.5	19.7 ± 0.3	58.5
6-700	8.9 ± 0.5	7.4 ± 0.5	1.6 ± 0.05	0.4 ± 0.01	0.5 ± 0.5	20.4 ± 0.3	60.8
	Melting Temperature 900 °C						
1-900 ^b	14.7 ± 0.5	14.6 ± 0.5	2.4 ± 0.05	0.7 ± 0.01	15.8 ± 0.5	12.0 ± 0.3	39.8
2-900 ^b	13.5 ± 0.5	13.3 ± 0.5	2.2 ± 0.05	0.6 ± 0.01	10.3 ± 0.5	14.0 ± 0.3	46.1
3-900	12.4 ± 0.5	12.1 ± 0.5	1.8 ± 0.05	0.6 ± 0.01	8.2 ± 0.5	15.5 ± 0.3	49.3
4-900	11.1 ± 0.5	9.6 ± 0.5	1.8 ± 0.05	0.5 ± 0.01	2.3 ± 0.5	18.1 ± 0.3	56.6
5-900	9.5 ± 0.5	9.4 ± 0.5	1.7 ± 0.05	0.4 ± 0.01	0.2 ± 0.5	19.2 ± 0.3	59.6
6-900	8.5 ± 0.5	8.4 ± 0.5	1.6 ± 0.05	0.4 ± 0.01	0.2 ± 0.5	20.2 ± 0.3	60.9

^a The elemental analyses were performed for all elements except for oxygen. The oxygen content is calculated on the basis of charge balance. ^b Devitrified samples.

(i.e. molar ratio $\text{NH}_4\text{H}_2\text{PO}_4/\text{MeCl}_2 \geq 2$). On the contrary, lead–cadmium glasses containing less than 50 mol % P_2O_5 retain fewer chloride than predicted by the model.

In Figure 2, the analyzed amounts of Pb, Cd, and Cl versus the P_2O_5 content in lead–cadmium phosphate glasses are compared with those predicted by the phosphate and water conversion model. This second model involves the reaction of residual chlorides with water and we can notice that experimental and calculated data are in very good accordance over the whole range of compositions investigated.

PbCl₂ + CdCl₂ + Alkaline Chlorides (NaCl+KCl) + NH₄H₂PO₄ Mixtures. Figure 3 presents the influence of the thermal treatment on the Pb, Cd, Cl amounts retained in the alkaline–heavy metal phosphate glasses versus P_2O_5 content. Raising the melting temperature from 700 to 900 °C and increasing the melting hold time from 30 min to 2 h does not lead to significant lead and cadmium losses. The chloride elimination is improved at 900 °C for P_2O_5 contents lower than 45 mol %.

In Figure 4, we can observe that the experimental analyses at 700 °C are best fitted by the phosphate conversion model. The difference between the two

models is indeed noticeable when one considers the amount of residual chlorides in the phosphate matrix.

The influence of the presence of alkaline chlorides on the conversion reaction at 900 °C is shown in Figure 5. When NaCl and KCl are present in the mixtures to be converted, the conversion reaction with water occurs only partially and the analyzed amounts of residual chlorides in x-900 glasses are intermediate between those calculated with the two models. Moreover, we can observe that the measured lead concentration is lower than that calculated by both models, which means that some lead is lost from the batch by volatilization.

Discussion

Our results show that the conversion into phosphate glasses involves two groups of chemical reactions (1–3 and 4–6), depending on the batch composition. If there is an excess of ammonium dihydrogen phosphate in the batch to be converted, compared to the stoichiometric reaction 1, the experimental results fit those calculated with the phosphate conversion model, which describes the conversion as the reaction of MCl_2 ($\text{M} = \text{Pb}, \text{Cd}$) with $\text{NH}_4\text{H}_2\text{PO}_4$ only (reactions 1–3). However, if there is an

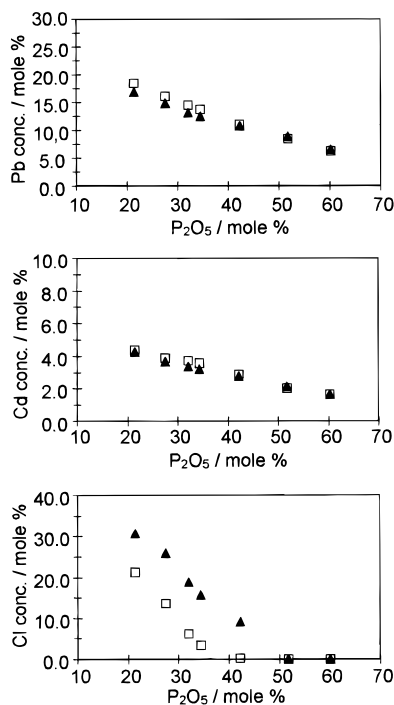


Figure 1. Pb, Cd, Cl concentrations, versus P_2O_5 content, in lead-cadmium phosphate glasses, obtained by elemental analyses (\square) and calculated with the phosphate conversion model (\blacktriangle). (Uncertainties are within the size of the symbols.)

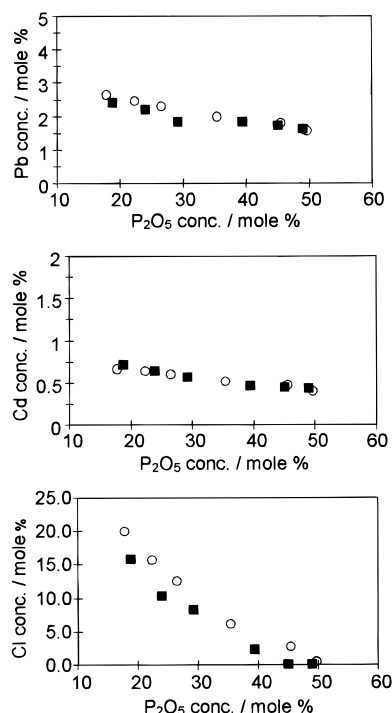


Figure 3. Influence of the thermal treatment on the Pb, Cd, Cl concentrations in the sodium, potassium, lead, and cadmium phosphate glasses versus P_2O_5 content: 700 °C, \bullet ; 900 °C, (Uncertainties are within the size of the symbols.)

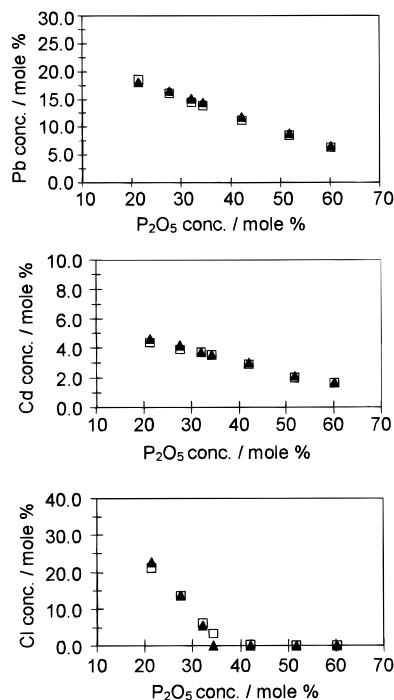


Figure 2. Pb, Cd, Cl concentrations, versus P_2O_5 content, in lead-cadmium phosphate glasses, obtained by elemental analyses (\square) and calculated with the phosphate and water conversion model (\blacktriangle). (Uncertainties are within the size of the symbols.)

excess of chloride compounds in the initial batch, compared to the stoichiometric reaction 1, the conversion mechanism also involves the reaction of $PbCl_2$ and $CdCl_2$ with the water generated during the thermal degradation of ammonium dihydrogen phosphate (reactions 4–6). In this last case, the chloride elimination

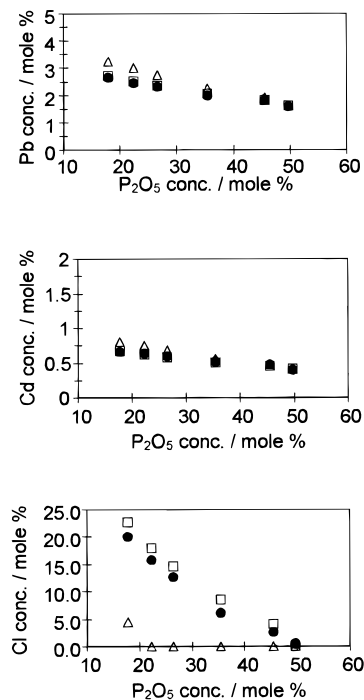


Figure 4. Pb, Cd, Cl concentrations, versus P_2O_5 content, in the sodium, potassium, lead, and cadmium phosphate glasses, obtained by melting at 700 °C (\bullet) and calculated with the two models (phosphate conversion model, \square ; phosphate and water conversion model, \triangle). (Uncertainties are within the size of the symbols.)

results in the volatilization of both ammonium chloride (NH_4Cl) and gaseous HCl. In both cases, the conversion reactions lead to the complete incorporation of lead and cadmium into the phosphate matrix, but the method

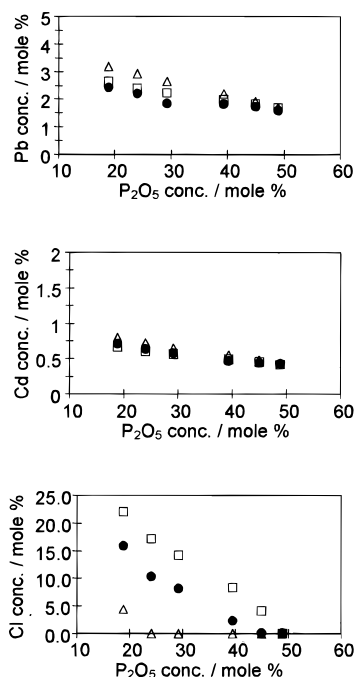


Figure 5. Pb, Cd, Cl concentrations, versus P_2O_5 content, in the sodium, potassium, lead, and cadmium phosphate glasses, obtained by melting at 900 °C (●) and calculated with the two models (phosphate conversion model, □; phosphate and water conversion model, △). (Uncertainties are within the size of the symbols.)

of chloride elimination depends on the composition of the batch.

The conversion of a more complex mixture containing $PbCl_2$, $CdCl_2$, $NaCl$, and KCl was also investigated. The glasses could be prepared at 700 °C, owing to the presence of alkali. This low temperature seems to be advantageous for limiting the volatilization losses of heavy metals. The lead concentration is indeed lower in glasses prepared at 900 °C, but the cadmium concentration does not significantly change when the glass melting temperature rises from 700 to 900 °C. Both glasses prepared at 700 and 900 °C contain a significant amount of residual chlorides (Figure 3). The experimental data for the glasses prepared at 700 °C are best fitted by the phosphate conversion model (Figure 4). At this temperature, the conversion reaction of chloride compounds into oxides with water does not participate significantly. This is in accordance with the results obtained by Verhulst et al.¹⁷ and Jakob et al.,¹⁸ who have reported the chemical reaction of water with chlorides in the 800–1000 °C range. Concerning phosphate glasses obtained by melting at 900 °C, Figure 5 shows that the amount of residual chlorides in the glasses containing less than 40 mol % of P_2O_5 is intermediate between those calculated with the phosphate conversion model and the phosphate and water conversion model. This is due to the incomplete conversion reaction of chloride compounds with water at 900 °C when alkaline chlorides ($NaCl$ and KCl) are added in the batches to be converted. Moreover, we can observe in Figure 5 that some lead volatilization losses occur at

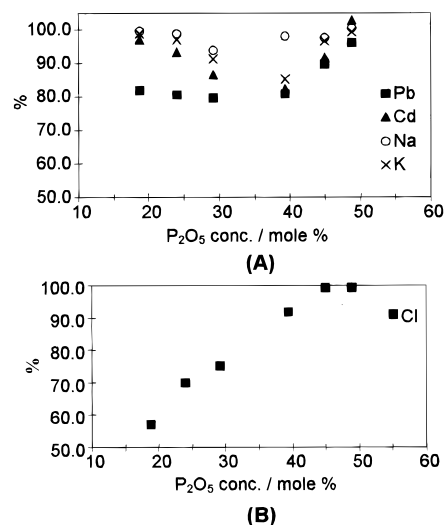


Figure 6. (A) Relative amounts of sodium, potassium, lead, and cadmium incorporated into phosphate glasses by the conversion process, versus P_2O_5 content in the glass. (B) Relative amounts of chloride eliminated by the conversion process versus P_2O_5 content in the glass.

900 °C in the same range of glass composition. This is attributed to the volatilization of lead chloride from the melt at 900 °C.

The occurrence of the high-temperature conversion reaction of lead chloride and cadmium chloride with water has been confirmed by the structural characterization of the resulting phosphate glasses.^{19,20} In particular, we have shown that the conversion reaction of chloride compounds with water induces the depolymerization of the phosphate glass network, because the phosphate and water conversion model implies that the MeO/P_2O_5 ratio in the glass increases with the amount of chloride compounds converted.

The presence of $NaCl$ and KCl in the batches reduces the range of batch composition for which chloride elimination is complete. We decided to estimate the efficiency of the phosphate conversion process applied to a $NaCl + KCl + PbCl_2 + CdCl_2$ mixture. It is evaluated by considering both the relative amounts of lead and cadmium incorporated into the glass matrix and the relative amount of eliminated chlorides (Figure 6). Over the whole range of composition investigated, more than 80% of the heavy metals introduced into the batches is incorporated into the phosphate matrix. Since the chloride elimination is total for P_2O_5 concentrations larger than 45 mol %, we can define a range of glass composition containing 45–50 mol % P_2O_5 (i.e. a molar ratio $NH_4H_2PO_4/\sum(\text{chloride compounds})$ ranging between 0.9 and 1.1), for which dechlorination and incorporation of lead and cadmium are optimum, $\geq 90\%$. Glasses with P_2O_5 concentration larger than 50 mol % have not been considered because they belong to the ultraphosphate composition, and ultraphosphate glasses have a very poor chemical durability.²¹

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