

Vitrified metal finishing wastes

I. Composition, density and chemical durability

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Abstract

Durable phosphate glasses were formed by vitrifying waste filter cakes from two metal finishing operations. Some melts formed crystalline components during cooling. Compositional analysis of dried, heat treated and vitrified samples was made using energy-dispersive X-ray spectroscopy, X-ray fluorescence spectroscopy, inductively-coupled plasma spectroscopy and Leco induction furnace combustion analysis. Hydrolytic dissolution, measured by an adapted product consistency test, was reduced by up to 3 orders of magnitude upon heat treatment or vitrification, surpassing the performance of borosilicate glass in some cases. This was attributed to the high levels of iron and zinc in the wastes, which greatly improve the durability of phosphate glasses. One of the wastes arose from a metal phosphating process and was particularly suitable for vitrification due to its high P_2O_5 content and favourable melting behaviour. The other waste, which arose from a number of processes, was less suitable as it had a low P_2O_5 content and during heating it emitted harmful corrosive gases and underwent violent reactions. Substantial volume reductions were obtained by heat treatment and vitrification of both wastes. Compositions and performances of some vitrified wastes were comparable with those of glasses which are under consideration for the immobilisation of toxic and nuclear wastes.

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1. Introduction

Vitrification is a favoured process for immobilisation and destruction of dangerous wastes, producing amorphous inorganic materials with high chemical durability [1,2]. The main glass-forming component of most vitrified wastes is SiO_2 . Other constituents are generally some mixture of Al_2O_3 , MgO , CaO , Na_2O , K_2O and Fe_2O_3 , often with lower levels of other oxides, halogens and sulphate. Silicate glasses, whose chemistry, physical properties and structure have been researched in depth over many years, are typically processed at temperatures of 1300–1600 °C [3–7]. However, the vitrification of non-silicate wastes has been studied in less detail.

Globally, the metal finishing industry generates millions of tonnes per annum (tpa) of solid waste. In USA, 450,000 tpa

of hazardous sludge is generated by the electroplating sub-sector alone [8]. These filter cakes and sludges are hazardous and their disposal is costly [8,9]. Suggested methods of disposal or recycling include plasma in-flight treatment [10,11], thermal bonding and slagging [12], metal recovery [13,14] and cementation [15,16]. A wide range of sludges and filter cakes arise, typically occurring as metal hydroxides with high water contents [9,10,17–20], which are precipitated from solution by alkali addition, usually $NaOH$ or $Ca(OH)_2$ [21].

Phosphating is a specific metal finishing process used to apply under-layers for sealed corrosion protection or paint finishes on metal articles [17,19]. Resulting wastes generally contain P_2O_5 equivalents of 15–50 wt.% [17,19,20,22]. Wastes arising from zinc plating or from a mixture of finishing operations, often contain less phosphorous and higher levels of metals such as zinc and chromium [9]. Reprocessing of phosphating waste has been carried out by mixing it with high levels of metallurgical dust and coke and reductively

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processing at high temperatures [14]. This method reclaims the zinc by volatilisation, but the other components remain wastes.

To our knowledge there is little published work regarding the vitrification of such wastes to form phosphate glasses, although some work on fibre glass formation is underway [23]. Some vitrified wastes do contain P_2O_5 , but at lower levels than SiO_2 , therefore these are classed as silicate wastes [24–31].

2. Experimental procedure and results

2.1. Analytical methods and waste material analysis

Samples of filter cake were obtained directly from the disposal facilities of two metal finishing operations, and were named waste B and waste P. Waste B was a pressed filter cake arising from mixed finishing operations including zinc plating. It occurred as a brown/green material with approximate dimensions 50–300 mm. Waste P was yellow sludge from a dedicated metal phosphating operation. It became powdery with a particle size of 0.1–2 mm when dried.

Table 1 shows the analysed compositions of the as-received materials. Inductively-coupled plasma optical emission spectroscopy (ICP-OES) measurements gave elemental analyses of solids and leachate solutions, and were carried out using an ARL 3410 spectrometer. Ion chromatography (IC) was used to analyse the sulphate and chloride contents

of leachate solutions. Carbon and sulphur contents of several samples were analysed using a Leco induction furnace combustion analyser. X-ray fluorescence spectroscopy (XRF) of every element with a molecular mass greater than sodium was carried out using a Bruker S4 Pioneer running a Uniquant program. A JEOL JSM6400 scanning electron microscope with Oxford energy-dispersive X-ray spectroscopy (EDS) facility was used for chemical analysis of all samples. These were measured at an accelerating voltage of 20 kV and identical magnification, sample distance, tilt angle and measurement time. A number of EDS measurements were made at different points on each sample, and these results were averaged. Water content was measured by weight loss upon drying (LOD) at 120 °C for 24 h. Loss on ignition (LOI) was measured by drying the wastes at 120 °C for 24 h then measuring weight loss after heating at 500 °C for 3 h. Values obtained from different techniques were used during normalisation where necessary, for example Na_2O contents determined by ICP-OES were used to normalise XRF and EDS results, and EDS results for other compounds (SO_3 , Cl, TiO_2 , MnO) were used to normalise ICP-OES results.

2.2. Heat treatments, glass batches and sample analyses

Samples B-1 and P-1 were generated by drying as-received wastes at 120 °C for 18 h. The resulting powders were sieved to <180 μm and stored in dry conditions. Sample B-1 required crushing prior to sieving.

Samples B-2 and P-2 were made by weighing 50 g of samples B-1 and P-1 into recrystallised Al_2O_3 crucibles. These were heated from 20 to 1000 °C over 4 h in an electric furnace, and held at 1000 °C for a further hour. Sample P-2 formed a molten liquid which was poured onto a steel plate and cooled. Sample B-2 remained solid. Thick fumes were evolved by heating waste B to 1000 °C. These emissions proved to be corrosive and were presumed to be predominantly HCl (see Section 3.1). Low levels of fumes were generated by heating sample P-1, but corrosive behaviour was not observed.

Formation of samples B-3, B-4, P-3 and P-4 involved mixing a phosphate precursor, analytical grade >99% purity ammonium di-hydrogen phosphate, $NH_4H_2PO_4$, with the wastes and subsequent vitrification. It was intended to use the dried waste samples, i.e. B-1 and P-1, for the production of the vitrified samples B-3, B-4, P-3 and P-4. In the case of waste P this was acceptable and a gentle melting action ensued. However, vitrification of mixtures B-3 and B-4 from sample B-1 led to violent reactions during melting. The heat-treated sample B-2 was therefore used as the starting material for samples B-3 and B-4, as most volatiles had been evolved so a less vigorous action was expected.

Batches to produce 50 g of samples B-3, B-4, P-3 and P-4 were calculated as shown in Table 2, weighed into sample bags using a 2 d.p. calibrated balance, and mixed. The added $NH_4H_2PO_4$ was calculated to bring the final P_2O_5 contents to >45 wt.%, near and into the expected glass forming region. Batches were placed in recrystallised Al_2O_3 crucibles and

Table 1
Compositional analysis of as-received waste materials

	Waste B (wt.%)		Waste P (wt.%)		
	XRF	ICP-OES	EDS	ICP-OES	EDS
Free H_2O		22.7			44.3
C		5.9			4.2
LOI		15.9			18.8
Li_2O	n/m ^a	n/m	n/m	0	n/m
B_2O_3	n/m	n/m	n/m	0	n/m
Na_2O	n/m	2.0	n/m	4.9	n/m
MgO	0	0.2	0.2	0	0
Al_2O_3	0.1	0.2	0.1	n/m	2.6
SiO_2	1.3	1.5	1.3	n/m	0.5
P_2O_5	3.9	5.4	3.9	45.3	36.2
SO_3	1.5	n/m	1.4	n/m	0.8
Cl	4.9	n/m	4.1	n/m	0
K_2O	0.1	0.2	0.2	0.7	0.8
CaO	0.3	0.2	0.2	1.3	1.6
TiO_2	0	n/m	0	n/m	0.6
Cr_2O_3	2.1	2.0	2.1	n/m	0
MnO	0.6	n/m	0.3	1.7	2.3
Fe_2O_3	28.2	28.7	28.1	35.5	40.6
NiO	0.4	0.3	0.3	0.9	0.8
ZnO	54.6	53.5	55.8	5.2	8.3
PbO	0	n/m	0	n/m	0
Total	98.0	94.2	98.0	95.5	95.1

^a n/m: not measured.

Table 2
Raw material mixtures for production of vitrified samples

Product	Precursor sample B-2		Precursor sample P-1		Precursor NH ₄ H ₂ PO ₄	
	g	wt.%	g	wt.%	g	wt.% P ₂ O ₅
Sample B-3	30	60	–	–	32.42	40
Sample B-4	25	50	–	–	40.52	50
Sample P-3	–	–	45	90	8.10	10
Sample P-4	–	–	40	80	16.21	20

heated in an electric furnace from 20 to 1100 °C over 4 h, and held at 1100 °C for a further hour. The molten liquids were poured onto a steel plate, cooled and annealed at 450 °C for 1 h, then cooled at 1 °C/min to room temperature and stored in dry conditions.

Samples B-3, B-4, P-2, P-3 and P-4 formed molten liquids at their processing temperatures. All formed dark black vitreous materials when cooled, and all samples except P-4 exhibited some crystallinity. Samples were analysed by EDS, as summarised in Table 3. It was not possible to accurately analyse Na₂O by EDS, so values obtained from ICP-OES analysis of samples B-1 and P-1 were used when normalising. This was not expected to introduce inaccuracy as the levels of Na₂O were low and any volatilisation would be minimised by the short melting times and low temperatures. There were concerns regarding the accuracy of EDS analysis of SO₃ at very low levels <0.5 wt.% due to the high phosphorous content and its masking effect on the sulphur K α peak. We measured the sulphur content of samples B-3, B-4, P-2, P-3 and P-4 by Leco analysis in addition to EDS. Leco results are shown as an SO₃ equivalent in brackets in Table 3.

2.3. Chemical durability measurements

Chemical durability was measured using an adapted version of ASTM C 1285-97, product consistency test B (PCT-B) [32]. This involves placing powdered samples in distilled water at 90 °C for 7 days. Handling and sample preparation procedures were followed, although a slightly different sieve fraction of 53–180 μ m, as opposed to 75–150 μ m, was used. Satisfactory removal of adherent fine particles from sample P-1 was difficult, so all samples were rinsed and decanted twice with distilled water, twice again with ethanol, then dried overnight. In order to evaluate the samples against a benchmark, the durability of a 5.3 wt.% Li₂O, 11.1 wt.% Na₂O, 21.9 wt.% B₂O₃, 61.7 wt.% SiO₂ glass, referred to as “MW” following [33], which is used as a vitrifying matrix for the immobilisation of high level nuclear waste, was measured. Glass MW was prepared by conventional melting techniques.

Sample weights of approximately 2 g were placed in 60 ml of distilled water in HDPE bottles, and held in a calibrated, fan-assisted oven at 90 °C for 7 days. The solutions were

Table 3
Summary of sample treatments, normalised compositions in wt.% from EDS, ICP-OES and Leco analyses, and major crystalline phases identified by XRD

Component	Analysis technique	Sample B-1 (dried, 18 h, 120 °C)	Sample B-2 (heated, 1 h, 1000 °C)	Sample B-3 (vitrified, 1 h, 1100 °C)	Sample B-4 (vitrified, 1 h, 1100 °C)	Sample P-1 (dried, 18 h, 120 °C)	Sample P-2 (heated, 1 h, 1000 °C)	Sample P-3 (vitrified, 1 h, 1100 °C)	Sample P-4 (vitrified, 1 h, 1100 °C)
ρ (g cm ⁻³)	Archimedes	1.18	4.53	3.10	3.57	1.37	3.26	3.00	3.12
H ₂ O	LOD	22.7	–	–	–	44.3	–	–	–
C	Leco	5.9	–	–	–	4.2	–	–	–
Na ₂ O	ICP-OES	2.0	2.0 ^a	1.2 ^a	1.0 ^a	4.9	4.9 ^a	4.4 ^a	3.9 ^a
MgO	EDS	0.2	0	0	0	0	0	0	0
Al ₂ O ₃	EDS	0.1	0	0.8	0.6	2.6	5.8	1.8	3.3
SiO ₂	EDS	1.3	1.4	1.1	1.2	0.5	0	0	0
P ₂ O ₅	EDS	3.9	2.2	35.5	43.7	36.2	32.8	43.8	51.0
SO ₃	EDS (Leco)	1.4	0.9	0.3 (0.02)	0.4 (0.05)	0.8	0.2 (0.04)	0.4 (0.03)	0.4 (0.03)
Cl	EDS	4.1	0	0	0	0	0	0	0
K ₂ O	EDS	0.2	0.2	0.1	0.2	0.8	0.8	0.7	0.6
CaO	EDS	0.2	0.3	0.2	0.3	1.6	2.6	2.1	1.8
TiO ₂	EDS	0	0	0	0	0.6	0	0.5	0.4
Cr ₂ O ₃	EDS	2.1	2.1	1.4	1.4	0	0	0	0
MnO	EDS	0.3	0.8	0.5	0.4	2.3	2.9	2.2	2.3
Fe ₂ O ₃	EDS	28.1	28.4	19.7	18.3	40.6	39.7	35.5	32.1
NiO	EDS	0.3	0.3	0.3	0.2	0.8	1.5	1.0	0.9
ZnO	EDS	55.8	61.5	39.0	32.6	8.3	8.8	7.7	6.5
Phase	XRD	ZnFe ₂ O ₄	ZnFe ₂ O ₄	AlPO ₄	AlPO ₄	Zn ₂ P ₂ O ₇	AlPO ₄	AlPO ₄	–
Phase	XRD	Fe ₃ O ₄	Fe ₃ O ₄	FePO ₄	–	Al ₂ O ₃	Fe ₂ O ₃	FePO ₄	–
Phase	XRD	–	ZnO	–	–	–	–	–	–

^a Estimated percentages based on ICP-OES analyses of samples B-1 and P-1.

Table 4
Adapted PCT solution analyses by pH, ICP-OES and IC

	MW	B-1	B-2	B-4	P-1	P-2	P-4
pH ± 0.03	10.37	6.95	6.84	5.84	3.06	6.91	7.03
Na ($\mu\text{g/ml}$)	682	324	174	11	625	6	10
P ($\mu\text{g/ml}$)	–	<1	<1	34	1045	2	6
S ($\mu\text{g/ml}$)	–	3	126	<1	4	<1	<1
Cl ($\mu\text{g/ml}$)	–	1110	18	3	13	20	4
K ($\mu\text{g/ml}$)	–	26	3	<1	1	<1	<1
Ca ($\mu\text{g/ml}$)	–	42	15	<1	2	<1	<1
Cr ($\mu\text{g/ml}$)	–	<1	<1	<1	<1	<1	<1
Mn ($\mu\text{g/ml}$)	–	2	<1	<1	110	<1	<1
Fe ($\mu\text{g/ml}$)	–	<1	<1	<1	<1	<1	<1
Ni ($\mu\text{g/ml}$)	–	1	<1	<1	87	<1	<1
Zn ($\mu\text{g/ml}$)	–	343	13	19	283	<1	<1
Si ($\mu\text{g/ml}$)	370	–	–	–	–	–	–
B ($\mu\text{g/ml}$)	529	–	–	–	–	–	–
Li ($\mu\text{g/ml}$)	175	–	–	–	–	–	–
Total ($\mu\text{g/ml}$)	1756	1851	349	68	2170	28	20

filtered and analysed by ICP-OES. Sulphate and chloride contents were analysed by IC. Sample blanks ensured baseline correction for each element. Results were normalised to 2 g sample/60 ml solution. Errors for ICP-OES become greater, as a fraction of the measured value, as the limit of detection for the instrument is approached. We estimate total errors of $\pm 30\%$ for leachate concentrations in the range 0–20 $\mu\text{g/ml}$, $\pm 20\%$ in the range 20–100 $\mu\text{g/ml}$, and $\pm 10\%$ at greater than 100 $\mu\text{g/ml}$. Solution pH was measured with a calibrated Hanna Piccolo 2 pH meter. The chemical durability of samples B-3 and P-3 were not measured as no significant differences from the other vitrified samples were expected. Results from the adapted PCT-B chemical durability tests are shown in Table 4 and Fig. 1. Fig. 1 illustrates the durability data with glass MW for comparison.

2.4. Density measurements

Density was measured by the Archimedes method. Samples were weighed using a calibrated 4 d.p. balance in air and

in water. Density was calculated using:

$$\text{Density} = \left(\frac{W_A}{W_A - W_W} \right) \times \delta_w \quad (1)$$

where W_A is the weight in air, W_W the weight in water and δ_w is the correction factor for the density of water at the measurement temperature, 22 °C. Sample weights in air for samples B-1, B-3, B-4, P-1, P-2, P-3 and P-4 were 3–9 g. Sample B-2 weighed only 0.5 g due to handling problems, so errors associated with its measurement were greater. Density results are shown in Table 3.

2.5. X-ray diffraction measurements

X-ray diffraction (XRD) spectroscopy was carried out using a Philips PW1730/10 goniometer with Co K α radiation. Spectra were measured at a rate of 6° 2 θ /h between 10° and 80° 2 θ . Identified phases are shown in Table 3.

3. Discussion

3.1. Waste analysis, processing, heat treatment and vitrification

Waste B contained high levels of zinc and iron but was low in phosphorous, whereas waste P was rich in phosphorous and iron, with a lower zinc content. Both compositions were typical of metal finishing wastes [17,19,20]. The water content of waste B was only half that of waste P, due to the use of a filter press. Drying the wastes gave large reductions in waste volume and mass. If this made the wastes sufficiently durable for landfill, it would provide cost savings. However the dissolution of samples B-1 and P-1 was still high so drying alone may not suffice.

Vitrified samples of both wastes contained slightly elevated levels of Al₂O₃ compared with as-received wastes due

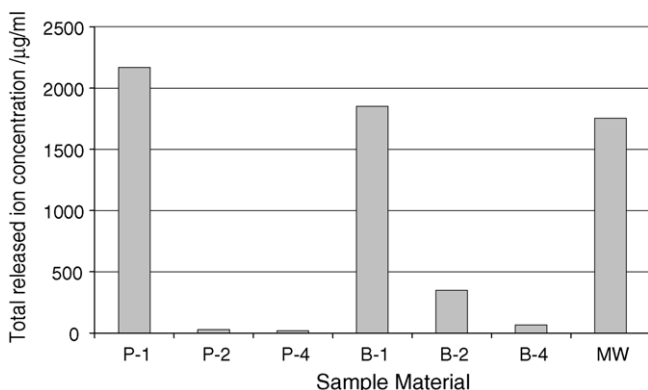


Fig. 1. Total normalised ion concentrations in the leachate.

to dissolution of Al_2O_3 from the crucible during melting. Refractory corrosion tends to be greatest at the glass/air boundary, and a corrosion meniscus could be seen in each crucible after melting. Alternative crucible materials such as zirconia or graphite may provide enhanced corrosion resistance. The aggression of the molten glass towards the melting vessel can affect the economic and practical aspects of large-scale melting of waste glasses. In answer to this problem, a number of alternative techniques have been developed for melting wastes. These include Joule-heated melters and cold-crucible induction melters [2].

XRD confirmed that only sample P-4 was fully amorphous. Major identified crystalline phases are listed in Table 3. Waste B mainly comprised zinc and iron compounds so the presence of ZnFe_2O_4 , Fe_3O_4 and ZnO in samples B-1 and B-2 was not unexpected. Addition of P_2O_5 and melting led to the formation of AlPO_4 and FePO_4 upon cooling of samples B-3 and B-4. Samples P-1 to P-3 all contained AlPO_4 , and the phases developed through the series P-1 to P-4 can be associated with the increasing P_2O_5 content, i.e. on increasing glass stability. It appears that AlPO_4 was readily crystallised from these melts, and may be a sensitive indicator of the level of P_2O_5 deficiency in these waste forms. The XRD studies will be discussed in more depth in a future publication.

The major components of phosphating wastes are phosphorous, zinc and iron, and these primarily determine the glass-forming region [17,19,20,22]. Mazurin et al. [34] collated a wealth of data on glass formation compositions for non-silicate glasses. Glasses based on the binary system P_2O_5 – Fe_2O_3 have recently received attention owing to their high chemical durability and their suitability as hosts for the immobilisation of certain nuclear wastes [35–44]. Investigations of third components in these glasses include ZnO [38,39], CaO [40], Na_2O and K_2O [41], PbO [42] and BaO [43]. This combined data suggested that stable glasses could be produced from wastes B and P providing the final product contained at least 40–50 wt.% P_2O_5 . This was therefore the range of additions chosen for our vitrification studies. The formation of vitreous products may still be possible with lower P_2O_5 equivalents, but there would be a high likelihood of crystallinity. Crystalline phases in vitrified wastes can be beneficial [26,27,29–31], although recent work indicated that crystallinity in certain iron phosphate glasses loaded with inactive simulated nuclear waste can reduce the chemical durability [44]. The merits of crystallinity are dependent upon the material application. If a vitrified waste is to be landfilled, crystallinity is not an issue provided it does not seriously impair chemical durability. If, on the other hand, the vitrified waste were used in the manufacture of other products, a tendency to crystallise could have serious implications.

The necessary addition of high levels of phosphate to vitrify waste B may have economic drawbacks. One alternative to phosphate may be to add silicate-based wastes such as incinerator ash, foundry sand or slag. Another alternative may be metal recovery rather than vitrification. Waste B was

rich in zinc, and processing technology exists for its recovery [13,14]. It is debatable whether recovery of iron by a similar process would be economically feasible owing to its relatively low value. Utilising the iron in these wastes to form durable glasses is a more attractive proposition. Consultation of the appropriate glass formation diagrams for phosphate and silicate glasses [34,45] indicated that glass formation in the systems P_2O_5 – Fe_2O_3 – ZnO and SiO_2 – Fe_2O_3 – ZnO should have been possible by adding approximately 40–50 wt.% of either P_2O_5 or SiO_2 to waste B. The results of this study indicate that, in the case of P_2O_5 , this was an oversimplification as no crystal-free glasses were formed in this range. It is believed that this was due to a combination of factors: increased Al_2O_3 contents from crucible dissolution, volatilisation of low levels of P_2O_5 during melting, and the complexity of the waste, i.e. the presence of other elements in addition to P, Zn and Fe. On the basis of these results we would expect to form a stable glass with 55–60 wt.% P_2O_5 addition, although further work would be required to confirm this. Alternatively an investigation of SiO_2 additions at 40–60% may be more worthwhile, although melting temperatures would probably increase. The addition of boron may also be worthy of technological consideration. Glass formation in the system B_2O_3 – P_2O_5 – ZnO occurs near 60% ZnO with 40% ($\text{B}_2\text{O}_3 + \text{P}_2\text{O}_5$), but only over a limited range [46]. Glass formation in the system B_2O_3 – P_2O_5 – Fe_2O_3 occurs at <30% Fe_2O_3 . Melting temperatures of 1200–1300 °C are expected. It therefore appears unlikely that the addition of B_2O_3 or ($\text{B}_2\text{O}_3 + \text{P}_2\text{O}_5$) could give any substantial advantage over the addition of P_2O_5 in terms of vitrification of waste P, owing to its high initial P and Fe contents. However, it may be possible to form stable glasses by adding B_2O_3 to waste B, and possibly at lower additions than would be required of P_2O_5 or SiO_2 . However, borate raw materials have high cost, and an economic balance may not be possible.

Untreated waste B contained approximately 5 wt.% Cl, which was problematic during high-temperature processing. Whilst heating waste B to 1000 °C, large amounts of visible fume were evolved. This fume attacked the furnace elements and corroded a thermocouple wire. It is likely this was caused by HCl generated from the waste material, as Cl was not detected in samples B-2 to B-4, so it was all evolved during heating. Evolution of SO_x also occurred during heating of waste B with further loss during vitrification, as shown in Tables 1 and 3. It was expected that carbonaceous material in both wastes would combust at high temperature, contributing to pollution through generation of CO_2 . The release of CO_2 , SO_x and chlorides into the atmosphere are strictly controlled by legislation [47]. To vitrify wastes high in chloride on a large scale would require abatement technology if the chloride cannot be immobilised in the solid product. In terms of waste B, its melting behaviour could also pose major problems. When dried, it formed hard lumps with average diameter 2–3 mm that were difficult to break up. When these were vitrified with $\text{NH}_4\text{H}_2\text{PO}_4$, the reaction during heating was violent, most of the mixture overflowed the crucible, and the

remaining product was inhomogeneous. Grinding and sieving of sample B-1 to a particle size of $<180\ \mu\text{m}$ gave satisfactory glass melting. Even this mixture reacted violently, but less so than with 2–3 mm waste particles. An additional process step was therefore required prior to vitrification of waste B. On a larger scale, this would generate dust that may require filtration.

Considering the potential practical and economic problems which vitrification of waste B plus P_2O_5 would present, we suggest that, on the basis of this study, it is not a viable option. However an alternative to P_2O_5 such as SiO_2 or another waste rich in SiO_2 may prove more successful.

Contrary to waste B, high temperature processing of waste P was successful. Dried waste P had a very low retention through a 1 mm sieve. It was easily handled and required no crushing. The powder was very light so it may be beneficial to add a little water as a binder to reduce dust during handling. During high temperature processing, waste P melted gently and remained within the crucible, with no violent reactions. Only a small amount of fume was observed, probably due to combustion of carbonaceous matter. Sulphate concentration in sample P-1 was higher than P-2, P-3 or P-4, so the fume may also contain SO_x , but study of the off-gas would be required to quantify this.

The behaviour of sample P-2 demonstrated that waste P forms a low viscosity liquid at 1000°C by itself with no P_2O_5 additions. Upon cooling, a black, amorphous material was formed with substantial crystallisation. Samples P-2 and P-3 also exhibited crystallinity, which was not unexpected since their final P_2O_5 contents were at the edge of the glass formation region [34]. The only fully vitreous material obtained during this study was sample P-4. The presence of crystallinity in vitrified waste P did not have a substantial effect on durability, as leachate concentrations were very similar from samples P-2 and P-4.

As with waste B, addition of SiO_2 and/or B_2O_3 to waste P may allow formation of stable glasses. However, consultation of glass data [34,45] indicated that the introduction of SiO_2 or B_2O_3 would not reduce the amount of P_2O_5 which must be added to form a glass. Adding SiO_2 would also increase glass-melting temperatures. The possibility of adding alternatives to P_2O_5 to waste P appears to be less viable than it does for waste B.

Heat treatment and vitrification of wastes B and P did not cause any substantial volatilisation of toxic chromium, nickel or zinc, based on the analyses in Table 3. This was encouraging, as reductive melting at similar temperatures can vapourise zinc, as discussed in Section 1.

Substantial volume reductions in both wastes were achieved by high temperature processing. Heat-treated and vitrified wastes had substantially higher densities than the untreated wastes. However additions of $\text{NH}_4\text{H}_2\text{PO}_4$ would at least partially offset any waste volume reductions. Vitrified samples, regardless of crystal content, generally had densities of $3\text{--}3.5\ \text{g cm}^{-3}$, typical of such materials [38,43].

On the basis of this study, we propose that the suitable compositional range to form stable crystal-free glasses from wastes P, B and similar metal finishing wastes is $55 \pm 5\ \text{wt.}\%$ P_2O_5 , $45 \pm 5\ \text{wt.}\%$ other oxides in the vitrified product. These totals exclude evolved components such as nitrates, carbonaceous materials and chlorides, and sulphate, which we have found to be largely insoluble in these glasses.

3.2. Chemical durability

High temperature processing of waste B, despite certain serious drawbacks, created highly durable products. Major leachants were Na, P, S, Cl, K, Ca and Zn. Heat treatment reduced the dissolution of Cl from the product by over 50 times, although this was due to the loss of Cl during heating. Dissolution of Na and Ca were decreased by approximately 50%, and K and Zn by over 90%. Sample B-4 contained nearly 50% P_2O_5 , so it was not unexpected that levels of P in solution were higher than for samples B-1 or B-2 where P_2O_5 was less than 5%. However, the level of dissolved P from sample B-4 was still low compared with total release from untreated waste B. Zinc dissolution increased slightly between samples B-2 and B-4, however leaching of S, Cl, Na, Ca and K was reduced. These reductions were greater than would be predicted simply on the basis that addition of 50% P_2O_5 diluted the contents by a factor of two, and even accounting for some further volatilisation of S and Cl during vitrification. This behaviour is attributed to the glassy matrix, which we conclude immobilises these elements safely. Leachate solutions from vitrified wastes were slightly more acidic. Assessment of the individual leachate components showed some balance between competing alkali and acidic components in solutions B-1 and B-2, whilst B-4 contained only phosphorous in any significant quantity, hence its solution had a lower pH. Although pH was lower, the alkali in solution was close to zero, showing a greatly improved durability from untreated waste B.

Reductions in waste P dissolution after heat treatment or vitrification were even greater than for waste B. Dissolution decreased by 2–3 orders of magnitude for each major leachate as shown in Table 4. Total measured leachate for samples P-2 and P-4 was 70–100 times lower than for P-1. In particular the dissolution of P, Na, Mn, Ni and Zn was dramatically reduced from the untreated waste. Durability was so high for these samples that most of the elements analysed in solution were below the limits of detection. The pH of the test solution changed dramatically for the three waste P durability samples. Untreated waste P produced an acidic solution, pH 3, whereas sample solutions P-2 and P-4 had neutral pH values. The dissolution of iron phosphate glass is slowed by a self-buffering effect [48,49]. This occurs because dissolved phosphate groups act to reduce pH, counteracting the effects of dissolved alkali and alkaline earth ions. It is beneficial because the corrosion rates of iron phosphate glasses are minimised in neutral and slightly acidic solutions [49]. The untreated waste, if landfilled, would

exert a stronger effect on its near-field environment owing to its more acidic pH. Either of the high temperature treatments would ensure minimal near-field interaction by comparison.

Heat treatment or vitrification of waste P was particularly successful in immobilising transition metals, which can pose serious health hazards [2]. Dissolution of Zn, Ni and Mn decreased from hundreds of micrograms per millilitre to below the limit of detection. This exceeds legislative requirements for landfill [1].

Total ion release from glass MW, a standard sodium–lithium–borosilicate glass used in the UK for high-level nuclear waste immobilisation, compared poorly with vitrified wastes B and P. This was somewhat surprising, as glass MW was developed to have high durability in addition to an acceptably low melting temperature $\sim 1250^\circ\text{C}$. The pH of MW leachate was 10.37, showing that this glass lacks the buffering action which occurs with iron phosphate glasses. Increased alkalinity modifies the corrosion rates of borosilicate glasses similar in composition to MW [50]. Published PCT results for EA glass, a standard US borosilicate glass used for nuclear waste immobilisation, also showed poor durability in comparison with samples B-2, B-4, P-2 and P-4 [51]. Although the conditions of the adapted PCT-B used in this study were slightly different to the standard PCT, the results still compare very favourably with those for borosilicate nuclear waste glass compositions. Vitrified wastes B and P even performed comparably with some ultra-durable iron phosphate glasses which were developed for immobilising special wastes [48,49,51]. The limited number of rinses during sample preparation in this study would increase dissolution rather than decrease it, since the presence of adherent fine particles would increase total surface area. This justifies the broad comparison of our results with those from the standard PCT despite slight differences in test parameters. Although a wider particle size range was used in the current test, both ranges were centred on the same particle size. Total ion release from heat treated and vitrified wastes B-2, B-4, P-2 and P-4, as measured by the adapted PCT-B, was generally 1–2 orders of magnitude lower than glass MW. Only the untreated wastes, B-1 and P-1 exhibited higher dissolution rates than glass MW.

All vitrified samples contained ≤ 0.05 wt.% SO_3 as measured by Leco analysis, showing that these materials have very low sulphate solubility. The vast majority of sulphate in the starting materials was evolved during heating or lost by volatilisation from the melt. Recent work established that the solubility of SO_3 in binary P_2O_5 – Fe_2O_3 glasses is < 0.1 wt.% [52], but glasses in the system P_2O_5 – ZnO – R_2O (R: Li, Na, K) can accommodate at least 15 wt.% SO_3 [53,54]. These two systems possess very different glass structures, and this explains the discrepancy. The vitrified wastes in this study were structurally similar to iron phosphates. Their negligible sulphate solubility underlines this relationship. The structure of phosphate glass is based around corner-sharing $(\text{PO}_4)^{3-}$ tetrahedra, which form rings or chains linked by P–O–P bonds. These are susceptible to hydrolysis, hence the low

chemical durability of many phosphate glasses [55,56]. The addition of network-modifiers, as evidenced by an increase in [O]/[P] ratio, causes depolymerisation of the network, breaking the P–O–P links to form P–O–M links, where non-bridging oxygens (NBOs) are coordinated by modifier ions. At high iron contents the phosphate tetrahedra are present largely as dimer $(\text{P}_2\text{O}_7)^{4-}$ units linked by octahedrally-coordinated Fe ions [38]. As a result, only a small fraction of oxygens participate in P–O–P bonds [49], hence the particularly high chemical durability of iron phosphate glasses. Phosphate glasses containing high levels of zinc can also exhibit good durability [56]. This can be attributed to the ability of zinc to depolymerise phosphate networks, a lower Zn^{2+} coordination number than many modifiers, the high electrostatic field strength of Zn^{2+} and the covalency of P–O–Zn bonds [53,57]. Divalent cations such as Ca^{2+} and Zn^{2+} form ionic cross-links between NBOs in separate phosphate chains, demonstrated in the improvement in chemical durability caused by adding zinc to sodium phosphate glasses [58]. The addition of alkali ions to zinc pyrophosphate glasses also improves durability. This was attributed to a shift in the equilibrium from two NBOs per phosphate tetrahedron towards three NBOs per phosphate tetrahedron, i.e. fewer P–O–P bonds [59].

Durability results for the glassy wastes B-4, P-2 and P-4 were consistent with previous work on zinc-iron phosphate glasses, in that the material with the higher iron content exhibited superior chemical durability [38,39]. This earlier work has shown that the aqueous dissolution rate of P_2O_5 – ZnO – Fe_2O_3 glasses decreases dramatically when Fe_2O_3 content increases from 10 to 40 mol%. The presence of phosphorous, iron, zinc, calcium and sodium in the glasses in this study indicates the expected glass structure would be highly depolymerised with some cross-linking. Waste P glasses, owing to their higher iron contents, would be expected to exhibit even more depolymerised structures than waste B glasses. Their superior chemical durability was taken as evidence of this structural behaviour.

The composition and properties of vitrified finishing wastes, particularly sample P-4, means they may find applications which could utilise their unique properties. In addition to exceptionally high chemical durability, these properties include relatively low glass transition temperatures and melting temperatures [34–36,38,41], thermal expansion coefficients comparable with silicate glasses [34], and high electrical conductivity [60].

4. Conclusions

Two metal finishing wastes have been chemically analysed following drying, heat treatment at 1000°C and vitrification with addition of phosphate precursors at 1100°C . Waste P was more suitable for direct vitrification than waste B on the basis of higher P_2O_5 content, fewer processing steps, favourable high-temperature behaviour and lower emissions.

Given that waste P arose purely from a phosphating process, whereas waste B arose from a number of metal finishing processes, there would seem to be clear advantages in keeping the wastes from such processes separate from each other.

The heat-treated and vitrified materials based on waste P meet any reasonable durability requirement for landfill, and would fill only half the volume of untreated waste. Vitrified waste B also performed well, however practical and economic issues may affect the feasibility of this process route. Alternatives to P₂O₅ addition were suggested which may allow more viable treatment of waste B. All heat-treated materials performed well in comparison with glass MW, a borosilicate glass used for the immobilisation of nuclear wastes. In particular the durability of the vitrified wastes was exceptionally high.

The addition of 20 wt.% P₂O₅ to waste P generated a crystal-free glass with excellent chemical durability. Rather than being landfilled, waste P could be utilised in a number of possible applications owing to the unique and interesting properties of glasses made from it. Examples include a major raw material in production of glasses for the immobilisation of other toxic wastes and glass fibre insulation.

Although this study examined the vitrification of two specific metal finishing wastes, their compositions were similar to metal finishing wastes reported by other workers. It seems reasonable to suggest that other wastes with similarly high iron and phosphate contents will be suitable for phosphate vitrification leading to potentially useful phosphate glasses.

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References

- [1] M. Krauss, Vitrification of waste materials, *Glastech. Ber. Glass Sci. Technol.* 70 (1997) 375–381.
- [2] P. Colombo, G. Brusatin, E. Bernardo, G. Scarinci, Inertization and reuse of waste materials by vitrification and fabrication of glass-based products, *Curr. Opin. Solid State Mater. Sci.* 7 (2003) 225–239.
- [3] M.B. Volf, *Glass Science and Technology, Chemical Approach to Glass*, vol. 7, Elsevier, New York, 1984.
- [4] M.B. Volf, *Technical Glasses*, Sir Isaac Pitman & Sons Publishers, London, 1961.
- [5] H. Rawson, *Inorganic Glass-Forming Systems*, Academic Press, London, 1967.
- [6] G.W. Morey, *Properties of Glass*, American Chemical Society, Reinhold Publishing Corp., New York, 1938.
- [7] J.E. Stanworth, *Physical Properties of Glass*, Oxford University Press, Oxford, 1950.
- [8] Technologies for Metal Recovery Save Energy and Reduce Toxic Metal Wastes, DOE/CH10093-266/DE94000251, DoE, USA 1994, <http://es.epa.gov/techinfo/facts/technlg.html>.
- [9] J. Viguri, A. Andres, C. Ruiz, F. Castro, Cement-waste and clay-waste derived products from metal hydroxides wastes—environmental characterisation, *Trans. IChemE* 79 B (2001) 38–44.
- [10] K. Ramachandran, N. Kikukawa, Plasma in-flight treatment of electroplating sludge, *Vacuum* 59 (2000) 244–251.
- [11] K. Ramachandran, N. Kikukawa, Thermal plasma in-flight treatment of electroplating sludge, *IEEE Trans. Plasma Sci.* 30 (2002) 310–317.
- [12] Fact Sheet on Disposal Options for Electroplating Sludge, City of Los Angeles, Board of Public Works, USA, <http://es.epa.gov/techinfo/facts/ca-htm/sludg-fs.html>.
- [13] C.J. Baldy, Recycling zinc phosphate sludge, *Met. Finish.* 94 (1996) 23–24.
- [14] W. Fennemann, R. Kola, D. Jentsch, Removal of zinc from phosphating process sludges, U.S. Patent No. 5,198,020, March 1993.
- [15] A.K. Minocha, N. Jain, C.L. Verma, Effect of inorganic materials on the solidification of heavy metal sludge, *Cem. Concr. Res.* 33 (2003) 1695–1701.
- [16] J. Viguri, A. Andres, R. Ibanez, C. Ruiz Puente, A. Irabien, Characterisation of metal finishing sludges: influence of the pH, *J. Hazard. Mater.* A 79 (2000) 63–75.
- [17] H.M. West, J. Cawley, R. Wills, Analysis and characterisation of water treatment plant sludges by X-ray fluorescence spectrometry, *Analyst* 120 (1995) 1267–1271.
- [18] R.R. Odle, I. Martinez, L.A. Deets, The recycling of hazardous metal plating wastes, *JOM* 43 (June) (1991) 28–31.
- [19] Nickel and Nitrite-Free Pretreatment for Car Bodies, <http://www.pfonline.com/articles/109704.html>.
- [20] J. Caponero, J.A.S. Tenorio, Laboratory testing of the use of phosphate-coating sludge in cement clinker, *Res. Cons. Recycl.* 29 (2000) 169–179.
- [21] D.C.R. Espinosa, J.A.S. Tenorio, Thermal behaviour of chromium electroplating sludge, *Waste Manage.* 21 (2001) 405–410.
- [22] R.F. Waters, H.E. Powell, L.N. Ballard, Recovery of metals and phosphate from waste phosphate sludge, U.S. Patent No. 3,653,875, April 1972.
- [23] OSWER Innovations Pilot: Industrial Phosphate Sludge Waste as a Raw Material for Iron Phosphate Glass, EPA 500-F-03-008, 2003, <http://www.epa.gov/oswer/docs/iwg/Phosphatefinal.pdf>.
- [24] M. Ozaki, H. Watanabe, B. Wiebusch, Characteristics of heavy metal release from incinerated ash, melted slag and their re-products, *Water Sci. Technol.* 36 (1997) 267–274.
- [25] Y.J. Park, S.O. Moon, J. Heo, Crystalline phase control of glass ceramics obtained from sewage sludge fly ash, *Ceram. Int.* 29 (2003) 223–227.
- [26] A.R. Boccaccini, M. Kopf, W. Stumpfe, Glass-ceramics from filter dusts from waste incinerators, *Ceram. Int.* 21 (1995) 231–235.
- [27] M. Romero, J.M. Rincon, R.D. Rawlings, A.R. Boccaccini, Use of vitrified urban incinerator waste as raw material for production of sintered glass ceramics, *Mater. Res. Bull.* 36 (2001) 383–395.
- [28] Y.J. Park, J. Heo, Vitrification of fly ash from municipal solid waste incinerator, *J. Hazard. Mater. B* 91 (2002) 83–93.
- [29] H. Endo, Y. Nagayoshi, K. Suzuki, Production of glass ceramics from sewage sludge, *Water Sci. Technol.* 36 (1997) 235–241.
- [30] S. Suzuki, M. Tanaka, T. Kaneko, Glass-ceramic from sewage sludge ash, *J. Mater. Sci.* 32 (1997) 1775–1779.
- [31] A. Gorokhovskiy, J.I. Escalante-Garcia, V. Gorokhovskiy, D. Mescheryakov, Inorganic wastes in the manufacture of glass and glass-ceramics: quartz-feldspar waste of ore refining, metallurgical slag, limestone dust and phosphorous slurry, *J. Am. Ceram. Soc.* 85 (2002) 285–287.
- [32] ASTM C 1285-97, Standard test methods for determining chemical durability of nuclear, hazardous and mixed waste glasses: the product consistency test (PCT).
- [33] I.W. Donald, B.L. Metcalfe, R.N.J. Taylor, The immobilisation of high level radioactive wastes using ceramics and glass, *J. Mater. Sci.* 32 (1997) 5851–5887.

- [34] O.V. Mazurin, T.P. Shvaiko-Shvaikovskaia, M.V. Streitsina, Handbook of Glass Data, Part D: Ternary Non-Silicate Glasses, Elsevier, New York, 1991.
- [35] D.E. Day, Iron phosphate compositions for containment of hazardous metal waste, U.S. Patent No. 5,750,824, May 1998.
- [36] X. Fang, C.S. Ray, A. Mogus-Milankovic, D.E. Day, Iron redox equilibrium, structure and properties of iron phosphate glasses, *J. Non-Cryst. Solids* 283 (2001) 162–172.
- [37] M. Karabulut, G.K. Marasinghe, C.S. Ray, D.E. Day, G.D. Waddill, C.H. Booth, P.G. Allen, J.J. Bucher, D.L. Caulder, D.K. Shuh, An investigation of the local iron environment in iron phosphate glasses having different Fe(II) concentrations, *J. Non-Cryst. Solids* 306 (2002) 182–192.
- [38] T. Jermoumi, M. Hafid, N. Niegisch, M. Mennig, A. Sabir, N. Toreis, Properties of $(0.5 - x)\text{Zn} - x\text{Fe}_2\text{O}_3 - 0.5\text{P}_2\text{O}_5$ glasses, *Mater. Res. Bull.* 37 (2002) 49–57.
- [39] S.T. Reis, M. Karabulut, D.E. Day, Chemical durability and structure of zinc-iron phosphate glasses, *J. Non-Cryst. Solids* 292 (2001) 150–157.
- [40] B. Kumar, S. Lin, Redox state of iron and its related effects in the $\text{CaO} - \text{P}_2\text{O}_5 - \text{Fe}_2\text{O}_3$ glasses, *J. Am. Ceram. Soc.* 74 (1991) 226–228.
- [41] X. Fang, C.S. Ray, G.K. Marasinghe, D.E. Day, Properties of mixed Na_2O and K_2O iron phosphate glasses, *J. Non-Cryst. Solids* 263–264 (2000) 293–298.
- [42] P.Y. Shih, Properties and FTIR spectra of lead phosphate glasses for nuclear waste immobilisation, *Mater. Chem. Phys.* 80 (2003) 299–304.
- [43] T. Jermoumi, M. Hafid, N. Toreis, Density, thermal and FTIR analysis of $(50 - x)\text{BaO} - x\text{Fe}_2\text{O}_3 - 50\text{P}_2\text{O}_5$ glasses, *Phys. Chem. Glasses* 43 (2002) 129–132.
- [44] D.S. Kim, M.J. Schweiger, W.C. Buchmiller, J.D. Vienna, D.E. Day, D. Zhu, C.W. Kim, T.E. Day, T. Neidt, D.K. Peeler, T.B. Edwards, I.A. Reamer, R.J. Workman, Iron Phosphate Glass As An Alternative Waste-Form for Hanford LAW, PNNL 14251, 2003, http://www.pnl.gov/main/publications/external/technical_reports/PNNL-14251.pdf.
- [45] O.V. Mazurin, T.P. Shvaiko-Shvaikovskaia, M.V. Streitsina, Handbook of Glass Data, Part C: Ternary Silicate Glasses, Elsevier, New York, 1987.
- [46] G. Sedmale, Investigations of borophosphate glass-forming systems $\text{Me}_x\text{O}_y - \text{B}_2\text{O}_3 - \text{P}_2\text{O}_5$, *Latvian. Kim. Zurn.* 4 (1994) 420–434.
- [47] Integrated Pollution Prevention and Control (IPPC), Secretary of State's guidance for glass manufacturing activities with melting capacity more than 20 tonnes per day, DEFRA, UK, June 2003, <http://www.defra.gov.uk/environment/ppc/laippc/sg2.pdf>.
- [48] M.G. Mesko, D.E. Day, B.C. Bunker, Immobilization of CsCl and SrF_2 in iron phosphate glass, *Waste Manage.* 20 (2000) 271–278.
- [49] M.G. Mesko, D.E. Day, Immobilisation of spent nuclear fuel in iron phosphate glass, *J. Nucl. Mater.* 273 (1999) 27–36.
- [50] S. Gin, J.P. Mestre, SON 68 nuclear glass alteration kinetics between pH 7 and pH 11.5, *J. Nucl. Mater.* 295 (2001) 83–96.
- [51] C.W. Kim, D. Zhu, D.E. Day, Iron phosphate glasses for vitrifying sodium bearing waste, *Ceram. Trans.* 143 (2003) 329–336.
- [52] W.K. Kot, H. Gan, I.L. Pegg, Sulphur incorporation in waste glass melts of various compositions, *Ceram. Trans.* 107 (2000) 441–449.
- [53] S.V. Stefanovskii, F.A. Lifanov, Glasses for immobilisation of sulphate-containing radioactive wastes, *Sov. Radiochem.* 31 (1989) 746–751.
- [54] G.H. Beall, J.E. Pierson, Zinc sulfophosphate glasses, U.S. Patent No. 5,328,874, July 1994.
- [55] Y. Abe, H. Hosono, Phosphate glasses and glass-ceramics, in: T. Kanazawa (Ed.), *Inorganic Phosphate Materials*, Elsevier, Tokyo, 1989, pp. 247–281.
- [56] L. Montagne, G. Palavit, R. Delaval, Effect of ZnO on the properties of $(100 - x)(\text{NaPO}_3) - x\text{ZnO}$ glasses, *J. Non-Cryst. Solids* 223 (1998) 43–47.
- [57] F. Delahaye, L. Montagne, G. Palavit, J.C. Touray, P. Baillif, Acid dissolution of sodium-calcium metaphosphate glasses, *J. Non-Cryst. Solids* 242 (1998) 25–32.
- [58] B.C. Bunker, G.W. Arnold, J.A. Wilder, Phosphate glass dissolution in aqueous solutions, *J. Non-Cryst. Solids* 64 (1984) 291–316.
- [59] R.K. Brow, Review: the structure of simple phosphate glasses, *J. Non-Cryst. Solids* 263–264 (2000) 1–28.
- [60] A. Mogus-Milankovic, A. Santic, M. Karabulut, D.E. Day, Study of electrical properties of $\text{MoO}_3 - \text{Fe}_2\text{O}_3 - \text{P}_2\text{O}_5$ and $\text{SrO} - \text{Fe}_2\text{O}_3 - \text{P}_2\text{O}_5$ glasses by impedance spectroscopy. II, *J. Non-Cryst. Solids* 330 (2003) 128–141.