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Determination of chloride in the leachates of stabilised waste by ion chromatography and by a volumetric method

Analysis and comparison

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Abstract

This study investigates the determination of the total chloride content in the leachates of samples of stabilised municipal solid waste incinerator fly ash (Portland cement), using two different leaching methods. The chloride content of the leachates obtained by two different methods was analysed by ion chromatography and by a volumetric method.

The results obtained with the two methods are very similar, although the results obtained by the volumetric method were generally lower.

1. Introduction

The potential environmental hazard of waste materials varies greatly with wastes from different sources. Although the minimisation of waste production, and its elimination where possible, is the first priority, it is clear that it will not be possible to eliminate a number of significant types of waste. These will, nonetheless, have to be dealt with in an environmentally acceptable manner. Several such types of waste will require treatment before disposal, to minimise adverse environmental effects [1,2]. In some cases, tested wastes, suitably stabilised with Portland cement, for instance, can be used in the construction industry [3]. The problem here is the development of a standard method to verify the leach-

ability of hazardous substances from stabilised waste [4–6].

In view of the increased need for waste treatment, the methods evaluated in this paper will prove relevant to the Community Directive on Landfills of Waste Materials and to future regulations in the field of waste minimisation, treatment and use. A number of factors, such as the tortuosity factor and the retardation factor are considered in determining whether the stabilisation process has been correctly carried out. The retardation factor is a measure of the chemical retardation of a component of the product, and the chloride ion is useful in evaluating this factor [7,8].

In this paper the results of two different methods to determine chloride are compared. One is a very fast and easy to perform volumetric method and the other a more accurate chromatographic method.

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Two different chloride release tests are also compared, one with liquid phase renewal [9] and the other based on a single extraction [10].

2. Materials and methods

The specimens were 4 cm cubes composed of very rapid-hardening Portland cement produced with fly ash from a municipal solid waste incinerator (MSWI), natural sand and water. Their composition was: Portland cement class C (540 kg/m³), MSWI fly ash (210 kg/m³), natural sand (0.5–1 mm, 560 kg/m³), silver sand (125–500 μ m, 560 kg/m³) and water (300 kg/m³).

Three separate, identically composed samples were analysed: T1, T2 and T3.

The leaching tests used were:

Test A [acetic acid extraction (AAT)]: extraction by 24-h immersion in an aqueous solution at pH 5.0 \pm 0.2 of acetic acid (0.5 M) with continuous agitation at a controlled temperature with a sample/extracting solution mass ratio of 1:16. The pH was controlled throughout the test (initially every 30 min) and kept at 5.0 \pm 0.2 by adding 0.5 M acetic acid solution. At the end of the test the leachate was filtered.

Test B [tank leaching test (TLT)]: extraction with water and replacement of the water after 2, 8, 24, 48, 72, 102, 168 and 384 h (8 steps), with a sample extracting solution mass ratio of 1:5, at a controlled temperature without agitation. The pH was not measured during the test, but at the end of each extraction step the leachate obtained was filtered and after measurement of the pH acidified to pH 2. Part of the sample was kept unacidified for the analysis of sulphates, bromides and chlorides.

The concentration of chloride ions was determined in the elution solutions after decanting and/or centrifugation to obtain a solution without suspended particles.

Two analytical techniques were used: ion chromatography and titration by a volumetric method.

The analysis was conducted using a Dionex 2000 i/SP ion chromatograph with a single pump

for the eluent (isocratic), with an analytical column, a guard column and chemical suppression of the eluent's conductivity. The working parameters were: analytical column: Dionex Ion Pac A S4 A (250 \times 4 mm) composed of a 16- μ m polystyrene–divinylbenzene substrate agglomerated with anion-exchange latex which had been completely aminated; guard column: Ion Pac A G4 G (50 \times 4 mm); column pressure: 970 p.s.i. (1 p.s.i. = 6894.76 Pa); eluent: 1.8 mM Na₂CO₃/1.7 mM NaHCO₃; flow-rate: 2.0 ml/min; detection: suppressed conductivity at 30 μ S FS; standard: 50 μ l chloride ions 2.0 mg/l; sample loop volume: 50 μ l.

The Mohr method was adopted with 0.1 M silver nitrate as titrant by detecting the final point by using 5% potassium chlorate as the indicator (pH 7–9).

3. Results and discussion

To determine the detection limits of the two methods used to determine the chloride concentration, under the conditions described above, a series of ten tests were carried out at decreasing concentrations. For each series the standard deviation was not to exceed \pm 0.70 for the chromatographic method and \pm 1.7 for the volumetric method.

Table 1 shows data on the five determinations of the chloride ion content by the chromatographic method and Table 2 by the volumetric method, for both the extraction methods (A and B). The extraction data for method A are subdivided into sections numbered 1–8, since the method requires eight steps.

An extraction process using long stirring periods is clearly better for solid samples such as the ones used.

It was, however, decided to measure the quantity of chloride ions released from the samples using two tests. Test A and B were chosen for two reasons: A is used in an international intercalibration test to evaluate the stabilization process for hazardous waste to minimize heavy metal release and B is currently used in Italy for the same purpose.

Table 1
Results of the analysis with the chromatographic method for the two elution tests

Sample	Chloride ion concentration (mg/l)	Mean (mg/l)	S.D. (mg/l)
<i>Test A</i>			
Blank-1	≤1.00, ≤1.00, ≤1.00, ≤1.00, ≤1.00		
T1-1	68.60, 65.80, 72.90, 69.80, 72.30	69.88	±2.58
T2-1	67.20, 73.90, 67.20, 67.20, 68.60	68.82	±2.90
T3-1	68.70, 69.90, 70.40, 66.80, 67.10	68.52	±1.61
Blank-2	≤1.00, ≤1.00, ≤1.00, ≤1.00, ≤1.00		
T1-2	68.10, 68.40, 68.80, 69.70, 67.40	68.48	±0.85
T2-2	61.70, 60.10, 63.50, 64.10, 63.50	62.58	±1.65
T3-2	81.50, 81.50, 79.90, 66.40, 67.40	75.34	±7.74
Blank-3	≤1.00, ≤1.00, ≤1.00, ≤1.00, ≤1.00		
T1-3	101.70, 102.00, 103.20, 102.60, 106.60	103.22	±1.97
T2-3	101.70, 102.50, 106.60, 106.60, 109.40	105.36	±3.20
T3-3	102.50, 102.00, 97.70, 100.00, 97.40	100.12	±2.16
Blank-4	≤1.00, ≤1.00, ≤1.00, ≤1.00, ≤1.00		
T1-4	101.70, 102.00, 102.70, 106.60, 108.00	104.20	±2.89
T2-4	102.00, 102.50, 95.40, 95.40, 96.00	98.26	±3.65
T3-4	102.50, 101.70, 95.40, 99.40, 97.40	99.28	±2.95
Blank-5	≤1.00, ≤1.00, ≤1.00, ≤1.00, ≤1.00		
T1-5	75.00, 74.20, 83.40, 84.60, 84.60	80.36	±5.28
T2-5	79.20, 80.10, 81.80, 73.40, 72.00	77.30	±4.33
T3-5	84.20, 85.00, 74.70, 72.60, 75.40	78.30	±5.77
Blank-6	≤1.00, ≤1.00, ≤1.00, ≤1.00, ≤1.00		
T1-6	82.50, 83.70, 81.40, 81.40, 82.60	82.32	±0.96
T2-6	82.50, 81.70, 77.10, 75.80, 70.60	77.54	±4.83
T3-6	78.70, 79.20, 70.00, 68.60, 70.00	73.30	±5.19
Blank-7	≤1.00, ≤1.00, ≤1.00, ≤1.00, ≤1.00		
T1-7	132.80, 135.60, 141.60, 131.40, 132.80	134.84	±1.99
T2-7	146.00, 143.70, 141.60, 140.90, 143.60	143.16	±2.08
T3-7	146.10, 143.00, 141.50, 138.40, 138.00	141.40	±2.53
Blank-8	≤1.00, ≤1.00, ≤1.00, ≤1.00, ≤1.00		
T1-8	289.60, 290.00, 289.90, 284.00, 292.70	289.24	±3.22
T2-8	283.80, 279.20, 286.90, 284.70, 284.70	283.88	±2.92
T3-8	282.70, 282.70, 281.00, 281.70, 281.80	281.98	±0.89
<i>Test B</i>			
Blank	≤1.00, ≤1.00, ≤1.00, ≤1.00, ≤1.00		
T1	30.80, 30.80, 29.70, 28.60, 30.10	30.00	±0.91
T2	28.70, 28.70, 29.00, 28.30, 28.50	28.64	±0.26
T3	30.80, 30.10, 29.90, 31.00, 30.20	30.40	±0.47

Table 2
Results of the analysis with the volumetric method for the two elution tests

Sample	Chloride ion concentration (mg/l)	Mean (mg/l)	S.D. (mg/l)
<i>Test A</i>			
Blank-1	≤30.00, ≤30.00, ≤30.00, ≤30.00, ≤30.00		
T1-1	58.30, 62.45, 65.06, 64.99, 60.72	62.30	±2.89
T2-1	56.56, 56.70, 64.50, 64.36, 58.20	60.0	±4.04
T3-1	66.12, 67.96, 61.52, 60.25, 65.80	64.33	±3.28
Blank-2	≤30.00, ≤30.00, ≤30.00, ≤30.00, ≤30.00		
T1-2	54.57, 54.72, 60.53, 60.67, 58.65	57.83	±3.01
T2-2	56.56, 57.13, 54.43, 54.72, 60.21	56.61	±2.32
T3-2	57.76, 57.90, 54.29, 54.43, 59.76	56.83	±2.39
Blank-3	≤30.00, ≤30.00, ≤30.00, ≤30.00, ≤30.00		
T1-3	94.98, 94.13, 99.65, 100.65, 100.60	98.00	±3.18
T2-3	91.02, 90.87, 94.84, 94.27, 95.03	93.00	±2.37
T3-3	96.82, 96.68, 90.58, 90.44, 95.32	93.96	±3.21
Blank-4	≤30.00, ≤30.00, ≤30.00, ≤30.00, ≤30.00		
T1-4	107.17, 94.98, 86.61, 86.11, 102.61	95.50	±9.41
T2-4	94.41, 93.42, 86.19, 85.06, 96.01	91.02	±5.02
T3-4	94.13, 94.13, 85.95, 85.38, 86.70	89.26	±4.47
Blank-5	≤30.00, ≤30.00, ≤30.00, ≤30.00, ≤30.00		
T1-5	63.51, 63.65, 71.16, 69.19, 74.76	70.45	±6.89
T2-5	64.93, 63.51, 63.93, 64.07, 68.40	64.97	±1.99
T3-5	68.75, 75.00, 61.38, 62.23, 70.01	67.47	±5.69
Blank-6	≤30.00, ≤30.00, ≤30.00, ≤30.00, ≤30.00		
T1-6	73.86, 75.13, 65.49, 66.34, 69.40	70.04	±4.34
T2-6	74.56, 73.57, 66.34, 66.06, 70.20	70.15	±3.95
T3-6	73.15, 74.14, 63.79, 60.50, 60.50	66.56	±6.59
Blank-7	≤30.00, ≤30.00, ≤30.00, ≤30.00, ≤30.00		
T1-7	117.23, 117.23, 123.47, 123.47, 119.91	120.26	±3.13
T2-7	126.31, 125.74, 129.71, 129.00, 120.30	126.21	±3.71
T3-7	123.19, 124.04, 111.99, 111.56, 115.40	117.24	±6.59
Blank-8	≤30.00, ≤30.00, ≤30.00, ≤30.00, ≤30.00		
T1-8	236.17, 237.59, 243.68, 243.40, 240.40	240.25	±3.37
T2-8	235.32, 236.17, 227.38, 228.23, 229.55	231.33	±4.11
T3-8	241.56, 241.07, 215.47, 215.33, 228.38	228.36	±12.96
<i>Test B</i>			
Blank	≤30.00, ≤30.00, ≤30.00, ≤30.00, ≤30.00		
T1	31.60, 31.18, 31.76, 29.91, 30.30	30.95	±0.81
T2	30.46, 31.18, 30.46, 30.33, 29.91	30.47	±0.46
T3	30.90, 31.18, 30.46, 30.05, 29.80	30.49	±0.57

As can be seen from Tables 1 and 2, the chloride ion values obtained with test B were always lower than those obtained with test A, since the test B contact time was too short to reach maximum leaching. In fact the values of test A increased with extraction time and reached their maximum with step 8, where the total contact time was 384 h.

The chloride ion concentrations found by the chromatographic method and those found by the volumetric method were very similar, though the results obtained by the volumetric method were generally lower.

The results obtained by both methods were analysed using two statistical tests: the *t* test and the variance test:

The *variance test* for coupled data, applied to the results of elution tests A and B demonstrated that there is a significant difference between the two methods, with lower values obtained with the volumetric method ($F = 26.23$, $p < 0.0001$).

The *t test* for coupled data, applied to the results of elution tests A and B with the two analytical methods, confirmed the evaluation of the variance test ($t = 5.122$ with 23 liberty degrees, $p < 0.0001$).

4. Conclusions

The tank leaching test is a good method for characterizing the leaching behaviour of solids.

The volumetric method is one of extreme analytical simplicity, but its limitation is the subjective judgement required of the tester in determining the end point of titration. Also the volumetric method cannot be applied when high sensitivity is required or the amount of chloride is low (its optimal range is 1000–2500 ppm of chloride). For high concentrations and when a very rapid analysis is required, it is, however, a good solution, though the possibility of lower results must be kept in mind.

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