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X-ray fluorescence determination of the composition of ash from incineration of organochlorine wastes from direct chlorination of ethylene to 1,2-dichloroethane

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Ash forms during the thermal utilization of organochlorine wastes from the direct chlorination of ethylene to 1,2-dichloroethane in the production of vinyl chloride. The composition of ash collected at Karpatnaftochim Ltd. was determined by X-ray fluorescence spectrometry. The ash macrocomponents are Fe_2O_3 and $FeCl_3$, as well as magnesium and sodium chlorides. Based on the results of the determination of the ash macro composition, ways were proposed to solve technological problems of organochlorine waste utilization.

Organochlorine by-products / X-ray fluorescence spectrometry / Ash from organic waste incineration

Introduction

During thermal utilization of organochlorine waste (OCW) from direct chlorination of ethylene to 1,2-dichloroethane in the production of vinyl chloride at Karpatnaftochim Ltd., hydrochloric acid is regenerated and thermal energy is utilized by obtaining technological water vapor in a steam generator. The problem with the steam generator is clogging of the pipeline with dust ash. This clogging obliges stopping of the OCW combustion reactor and the steam generator for cleaning the hot combustion gas pipeline from ash. To solve this problem and ensure proper functioning of the steam generator, it is necessary to determine the chemical composition of the dust ash that clogs the pipeline, and to develop proposals for technological solutions of the problem.

It is known [1,2] that, among the methods of elemental analysis, X-ray fluorescence (XRF) spectrometry is a convenient and rapid method for determining the chemical composition of metal alloys, minerals and industrial products. Marjanovic *et al.* [3] determined macrocomponents such as Ca, Si, Mg, Al, and Fe, as well as microcomponents such as S, K, Ti, Na, P, Mn, and Sr, in cement by optical emission atomic spectral analysis with inductively coupled plasma (ICP-OES), using cement samples in the form of solutions and stabilized suspensions. Fig. 1 shows the relationship between the results of the ICP-OES method with the axial signal from the plasma for cement samples in the form of solutions, and of the method of XRF in the case of macrocomponents. The comparison confirms the conclusions of the paper [3] that the differences in the results are within acceptable limits with respect to the experimental error.

Guirado *et al.* [4] showed that for cements with high aluminum contents, the chemical composition, calculated in weight percent of phases, from X-ray diffraction using Rietveld's analysis well match the oxide compositions obtained by XRF. The XRF method was chosen to verify the calculation method and the correlation is shown on Fig. 2 for CES-100 cement showing the calculated mass percentages, considering an empirical correction according to three standards, for all phases with the exception of pleochroite.

Bosch Reig *et al.* [5], analyzing three oxides (Fe_2O_3 – 0.26%, SO_3 – 2.17%, K_2O – 0.09%), proved the possibility of applying the "additive-dilution" method (ADM) to an XRF-analysis of Portland cement, where cement of known composition was used as a standard. It was shown that small quantities can be determined by hyperbolic dependence between the intensity of the K_α-lines and the dilution factor. The relative error depends on the chemical element.

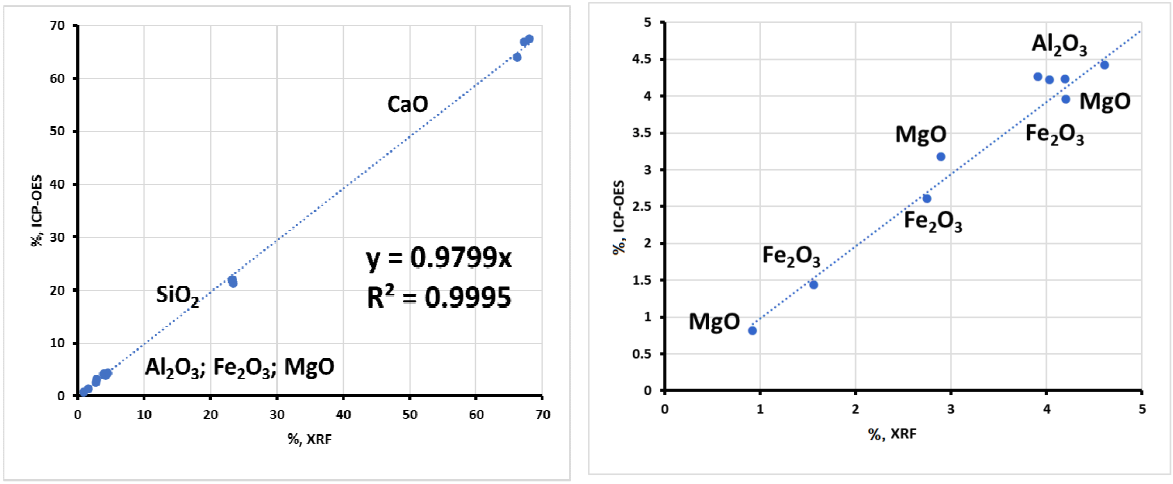

Fig. 1 Correlation between the results of the ICP-OES method with the axial signal from the plasma for cement samples in the form of solutions, and of the XRF method in the case of macrocomponents [3].

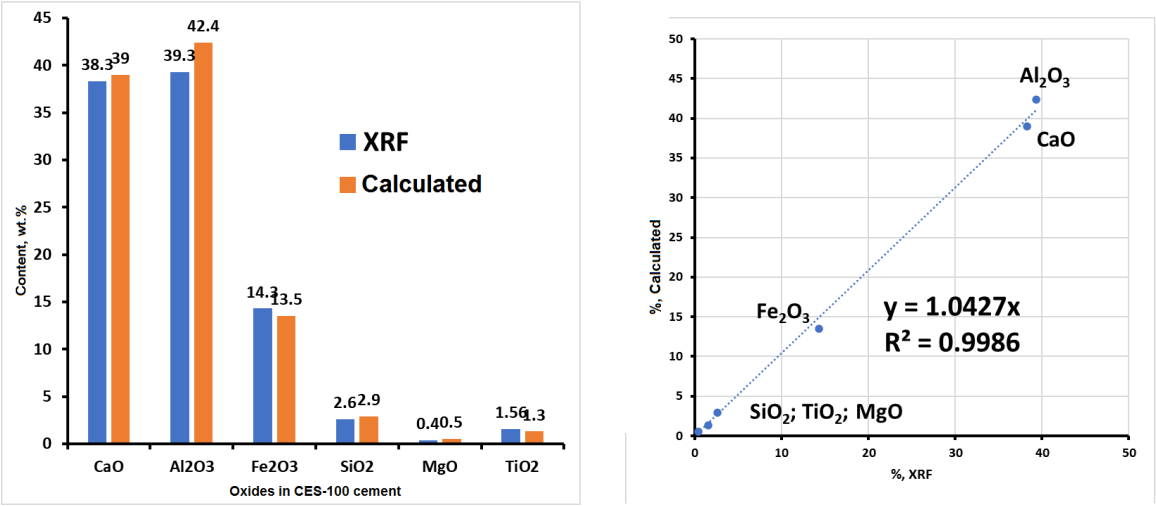

Fig. 2 Correlation between the results of the XRF method and the calculation method with empirical correction using three standards for CES-100 cement [4].

In the case of coal and ash obtained from flue gases, or remaining in the furnace after combustion of coal, at eight thermal power plants in India, the content of 18 elements was studied [6] by the energy-dispersive XRF-method. Quantitative determination of the elements was performed under optimal operating conditions for the following three groups: 1) Na, Mg, Al, Si, K, and Ca; 2) V, Cr, Mn, Fe, Co, Ni, Cu, and Zn; 3) As, Sr, Cd, and Pb. It may be noted that the ash mass reconstruction was achieved to 95% when presenting these elements in oxide forms. The remaining 5% is explained as organic compounds, sulfur compounds, P_2O_5, and TiO_2. Concerning the determination of As and Pb it was noted that lines of these elements have the same energies: L_α for Pb and K_α for As. The Pb concentration was calculated directly from the intensity of the L_β line. The As concentration was obtained from the ratio of the intensities of the L_α-line for Pb and the K_α-line for As.

In the case of ash from lignin combustion, which was taken from the electrostatic precipitator at a thermal power plant, the content of Sn, La, Ba, Sr, Zr, and Mo was determined [7] using the XRF-method with excitation by a radioactive source ^{241}Am. Note that in the original paper there are no units for concentration; probably it is wt.%, as used in previous works by the same authors (see for example [8]). Among the modern applications of the XRF-method for the analysis of ash from combustion, we note a quantitative determination [9] of traces of elements such as Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Cu, Zn, As, Rb, Sr, and Pb, by X-ray microfluorescence in particles with a size of 20-60 μm. An X-ray tube and synchrotron radiation were used for excitation and

showed the possibility of determining the composition of individual ash particles, provided that the particle size is proportional to or larger than the cross-sectional size of the excitation beam. According to the paper [9] the XRF-method provides detection limits of the elements at the level of 10-100 ppm when the atoms are excited by synchrotron radiation.

This paper presents the results of a determination by XRF-spectrometry of the composition of the ash formed during thermal OCW utilization from direct ethylene chlorination to 1,2-dichloroethane in the production of vinyl chloride at Karpatnaftochim Ltd. Information about the ash composition is needed to plan ways to solve technological problems of OCW utilization.

Experimental

The research object was solid ash, which clogs the gas pipeline between the combustion furnace and the steam generator. The analysis was performed according to the requirements of DSTU B V.2.7-202:2009. "Building materials. Cements and materials of cement production. Chemical analysis methods".

For the analysis 200 g of ash was ground and sieved through a sieve with a cell size of 0.1 mm. The sieved samples were dried for 4 h at a temperature of 150°C. After cooling in a desiccator, three samples were taken for analysis and placed into polyethylene cuvettes with a diameter of 32 mm, which were covered with a film of 4 µm Prolene® Thin-Film (Cat. No.: 416, Chemplex Industries, inc., USA). In each cuvette the ash layer was compacted using a hand press to a thickness of approximately 1 cm and then analyzed.

For the determination of the qualitative and quantitative ash macrocomposition by XRF-analysis an energy-dispersive XRF-spectrometer model ElvaX Light SDD was used (www.elvatech.com). The XRF-spectrometer was equipped with an X-ray tube with a Rh anode operating at a voltage of 50 kV and a Fast SSD detector, which provides a resolution of <140 eV for the Mn K_α-line.

The software for the analysis provides sequential recording of two spectra for: 1) heavy elements (without purging the chamber with helium) and 2) light elements (with purging the chamber with helium to increase the sensitivity to light elements Na, Mg, Al, Si, P, S). The recording time was 180 s. After recording the spectra, the qualitative composition of the sample was determined. For each element the quantitative content was calculated using device software according to the established list of elements.

For the quantitative evaluation of components in solid samples, calibration of the XRF-device was performed using a calibration mixture, the composition of which is given in Table 1. During the preparation of the samples for XRF-analysis it was observed that the ash samples were markedly hygroscopic.

Sodium determination was also performed by atomic emission spectrophotometry with a stoichiometric methane-air flame as the excitation source using a device model FPL-1 equipped with an interference filter with a light wavelength of (589 ± 5) nm.

Results and discussion

By XRF it was established that the ash sample consisted of the following main macrocomponents: iron, chlorine, sodium, magnesium, sulfur, and calcium, in the approximate ratios given in Table 2.

In industrial furnaces the OCW combustion is carried out at a temperature of 1200°C. Under these conditions, $FeCl_3$ (the main component of the ethylene chlorination catalyst) completely decomposes to Fe_2O_3, since such decomposition occurs, according to [10], already at 400°C. Sodium chloride (promoter in the catalyst) is thermally stable because it melts at 801°C and boils at 1413°C. Magnesium is not in the catalyst and its presence in the ash can be explained by the destruction of refractory materials of the inner lining of the furnace. Magnesium chloride, which can be formed by the interaction of the refractory surface with chlorine or hydrogen chloride, is also thermally stable because it melts at 714°C and boils at 1412°C. After heating of the ash at 800°C for 4 h, the weight loss of the sample was 25%. According to XRF, after the heating the chlorine content had decreased by a factor of 4.7, from 33% to 7%, and the iron content increased by a factor of 1.6, from 34% to 54% (Table 2). It is likely that during the pyrolysis of the ash in air, Cl_2 and/or hydrogen chloride is formed, possibly from the residue of highly chlorinated resinous products, which are in bottom residues of OCW.

Table 1 The composition of the calibration mixture for the XRF device.

Substance	Weight, g	Weight fraction, %	Element	Weight fraction, %
Fe_2O_3	0.9230	31.51	Fe	22.04
NaCl	1.4006	47.82	Na	18.80
MgO	0.3509	11.98	Cl	29.02
S	0.2545	8.69	Mg	7.23
Total	2.9290	100	S	8.69

Table 2 The composition of the ash before and after heating at 800°C.

Element	Ash composition according to XRF, wt.%	
	before heating	after heating at 800°C
Fe	33.52	54.31
Cl	32.69	6.63
Na	9.87	5.83
Mg	4.44	4.70
S	0.89	0.57
Ca	0.32	0.31
Total	81.74	72.35

Table 3 Composition (wt.%) by XRF of insoluble parts after extractions and dry residue of aqueous extraction for the ash from OCW combustion.

Element	Soluble part in water	Insoluble part in water	Insoluble part in acid
Fe	0.00	60.27	64.82
Cl	76.71	3.82	4.08
Na	11.47	2.12	0.33
Mg	6.04	3.80	1.05
S	0.78	0.24	0.09
Ca	0.68	0.06	0.05

The apparent decrease of the sodium content from 10% to 6% is probably due to the low sensitivity of the XRF method to this element and the relatively large errors. The deference in the element content from 100% can be attributed to oxygen, which is not analyzed by the XRF method. In the initial ash sample, according to XRF data, the molar ratio between the main elements was as follows: Mg : Na : Fe : Cl = 1 : 2.35 : 3.29 : 5.05. If assuming that NaCl and $MgCl_2$ are present in the ash in the form of thermally stable compounds, then the molar fraction of chlorine per ferric chloride will be 0.70. Consequently, the bulk of the iron in the ash is in the form of Fe_2O_3, at a molar ratio of iron in chloride and oxide of approximately 1:13.

For certain parts of the ash, extractions were carried out by water at 80°C and by boiling nitric acid (25%), both for one hour. In both cases, after filtration, a solution and an insoluble part were obtained. For the ash extraction by water and by nitric acid, the weight fraction of the undissolved part was 73% and 27%, respectively. An aliquot of the aqueous extract after evaporation and drying gave a dry residue. According to visual observations, the part that was insoluble in acid contained black carbon particles, apparently pyrolyzed organic substances, which had formed during the OCW combustion. The insoluble parts after the extractions and the dry residue were analyzed by XRF (Table 3).

According to the XRF data (Table 3) the insoluble parts after extractions by water and by acid contained a significant amount of iron, 60% and 65%, respectively. In the form of chloride ions chlorine has almost completely moved into the soluble part (77%) and the chlorine weight fraction according to the XRF-method in the insoluble parts is only 4% (Table 3), compared with 33% in the initial sample of the ash (Table 2). Sodium has almost completely moved into the soluble part (12%), and the sodium weight fraction in the insoluble in acid part, for example, is only 0.3%. The magnesium content in the soluble part (6%) is also higher than in the insoluble parts by about 1% and 4% for the acid and aqueous extractions, respectively. According to the XRF-analysis, similar ratios between the insoluble and soluble parts of the extractions were observed for calcium and sulfur.

The macroelement composition was recalculated according to the XRF-results to compounds in the following sequence: 1) weight fractions of $MgCl_2$ and NaCl; 2) the difference between the weight fraction for chlorine, determined by the XRF-method, and chlorine in NaCl and $MgCl_2$ is chlorine, which is accounted for as $FeCl_3$; 3) weight fraction of $FeCl_3$ for chlorine per $FeCl_3$; 4) Fe, which is accounted for as $FeCl_3$; 5) weight fraction of Fe_2O_3 in terms of Fe, which is defined as the difference between the total Fe content and the Fe amount in $FeCl_3$. Chlorine, which belongs to $FeCl_3$ can also be determined by the loss of weight by heating at 800°C, assuming that after heating Fe is present as Fe_2O_3. However, chlorine after heating is only 6.63%, and the balance for NaCl and $MgCl_2$ should be 8.99% + 13.71% = 22.70%. Table 4 shows the results of the calculation for the macrocomponent contents (wt.%) that were obtained by the XRF-method for the initial sample of the ash from OCW combustion, as well as for the ash after heating, and the ash part that is insoluble in acid.

Table 4 The macrocomponent contents (wt.%) calculated by XRF-method for the initial sample of the ash from OCW combustion, as well as for the ash after heating and the ash part that is insoluble in acid.

Compound	Starting ash	Starting ash with the results of flame photometry for sodium	The ash after heating at 800°C	The ash part that is insoluble in acid
NaCl	25.08	4.17	14.82	0.84
$MgCl_2$	17.39	17.39	18.41	4.11
$FeCl_3$	6.89	26.25	0.00	0.78
Fe_2O_3	44.53	34.99	77.63	92.27
Total	93.89	82.80	110.86	98.00

The sodium content determined by the method of flame photometry in the ash part that is soluble in water was obtained as 1.46%, which is significantly (7.86 times) less than by the XRF-method (11.47%). If we assume that the part of the ash that is soluble in acid corresponds to the composition of the initial ash, then we can compare the result of the sodium determination in this part by flame photometry (1.64%), and by the XRF-method for the initial ash as 9.87% (factor 6.02). The recalculation of the initial sample using flame photometry results for sodium in the acid extract was carried out in the sequence described above and the results are shown in Table 4.

It should be noted that Marjanovic *et al.* [3] observed good correlations (Fig. 1) between XRF and ICP-OES results, however, among the elements that were identified in the cement there was no sodium, for which the study presented in this paper shows significantly inflated results by the XRF-method compared to flame photometry. The final balance in Table 4 shows that the largest error in the results of the XRF-method is connected with the presence of light elements in the sample. In the part that is insoluble in acid, the contents of sodium and magnesium chlorides are much lower than in all the other samples and the total balance reaches 98%. It is also necessary to note that the results of the analysis by the XRF-method are significantly influenced by the sample matrix. Therefore, to achieve more accurate results, it is necessary to use the "dilution-addition" method, which was used in [5], but the time required for the analysis increases. In this study of the composition of the ash from OCW combustion, the obtained results are informative and suitable for further steps to solve the problem of clogging of the pipeline by dust ash.

One of the ways to solve the clogging of the gas pipeline by dust ash can be the extraction of the iron-containing catalyst from the OCW, as described in [11], or precipitation of iron as hydroxide. It is necessary to note that in both methods, sodium chloride, which is a promoter in the catalytic system, will migrate from the OCW organic phase into an aqueous solution. Different ways for picking up iron-containing catalyst components from OCW by extraction and precipitation methods can probably be combined to increase the extraction efficiency. When the iron-containing catalyst is removed from the OCW, the amount of ash will decrease by about a factor 5 and will mainly consist of magnesium chloride.

Conclusions

The composition of the ash formed during thermal utilization of OCW from direct ethylene chlorination to 1,2-dichloroethane in the production of vinyl chloride at Karpatnaftohim Ltd was determined by XRF-spectrometry. The ash macrocomponents are Fe_2O_3 and $FeCl_3$, as well as magnesium and sodium chlorides.

The results of the analysis by the XRF-method are significantly influenced by the sample matrix. It was found that the results for sodium as obtained by the XRF-method are significantly inflated in comparison with the results obtained by flame photometry. The total balance reached up to 98% when taking into account the results of the analysis of the ash part that is insoluble in acid, where the sodium and magnesium chloride contents were much lower. Even such semiquantitative results for the sodium content allow considering that the obtained ash composition is informative and suitable for further steps to solve the problem of clogging of the pipeline by dust ash.

To solve the technological problems of OCW utilization, according to the results of the determination of the ash macro composition, extraction of the iron-containing catalyst from the OCW or precipitation of iron as hydroxide were proposed. A combination of these methods could increase the extraction efficiency

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References

[1] H.R. Verma. *Atomic and Nuclear Analytical Methods: XRF, Mössbauer, XPS, NAA and Ion-Beam Spectroscopic Techniques*, Springer, 2007, 376 p.

[2] M.S. Shackley (Ed.), *X-ray Fluorescence Spectrometry (XRF) in Geoarchaeology*, Springer-Verlag, New York, 2011, 245 p.

[3] L. Marjanovic, R.I. McCrindle, B.M. Botha, J. Hermanus Potgieter, *J. Anal. At. Spectrom.* 15 (2000) 983-985. https://doi.org/10.1039/b003892j

[4] F. Guirado, S. Galí, S. Chinchón, *Cem. Concr. Res.* 30 (2000) 1023-1029. https://doi.org/10.1016/s0008-8846(00)00289-1

[5] F. Bosch Reig, V. Peris Martinez, J.V. Gimeno Adelantado, S. Sánchez Ramos, D.J. Yusá Marco, F. Bosch Mossi, *J. Anal. At. Spectrom.* 13 (1998) 583-585. https://doi.org/10.1039/a800582f

[6] M. Tiwari, S.K. Sahu, R.C. Bhangare, P.Y. Ajmal, G.G. Pandit, *Appl. Radiat. Isot.* 90 (2014) 53-57. https://doi.org/10.1016/j.apradiso.2014.03.002

[7] O. Dogan, M. Kobya, *J. Quant. Spectrosc. Radiat. Transfer* 101 (2006) 146-150. https://doi.org/10.1016/j.jqsrt.2005.11.072

[8] M. Ertuğrul, M. Kobya, O. Doğan, *J. Radioanal. Nucl. Chem.* 203 (1996) 119-123. https://doi.org/10.1007/bf02060386

[9] L. Vincze, A. Somogyi, J. Osán, B. Vekemans, S. Török, K. Janssens, F. Adams, *Anal. Chem.* 74 (2002) 1128-1135. https://doi.org/10.1021/ac010789b

[10] S.B. Kanungo, S.K. Mishra, *J. Therm. Anal.* 46 (1996) 1487-1500. https://doi.org/10.1007/bf01979262

[11] M. Shpariy, V. Starchevskyy, Z. Znak, R. Mnykh, I. Poliuzhyn, *East.-Eur. J. Enterp. Technol.* 2/10 (104) (2020) 19-26. https://doi.org/10.15587/1729-4061.2020.201696