ANALES de Edificación

Received: 27/2/2022
Accepted:06/3/2022

Anales de Edificación
Vol. 8, Nº1, 41-45 (2022)
ISSN: 2444-1309
Doi: 10.20868/ade.2022.5021

Una contribución a la economía circular: cenizas volantes de incineración de residuos sólidos urbanos para producir aglutinantes ecológicos
A contribution to the circular economy: municipal solid waste incineration fly ash to produce eco-friendly binders

Cristina Marieta[a]; Alexander Martín-Garín[b]; Iñigo León[c]; Ana Guerrero[d]

[a] Department of Chemical and Environmental Engineering, Faculty of Engineering of Gipuzkoa, University of the Basque Country, UPV/EHU, Plaza Europa 1, 20018 Donostia-San Sebastián, Spain; cristina.marieta@ehu.eus
[b] ENEDI Research Group, Department of Thermal Engineering, Faculty of Engineering of Gipuzkoa, University of the Basque Country, UPV/EHU, Plaza Europa 1, 20018 Donostia-San Sebastián, Spain; alexander.martin@ehu.eus
[c] Department of Architecture, Faculty of Engineering of Gipuzkoa, University of the Basque Country, UPV/EHU, Plaza Europa 1, 20018 Donostia-San Sebastián, Spain; inigo.leon@ehu.eus
[d] Eduardo Torroja Institute for Construction Sciences (IETcc-CSIC), C/ Serrano Galvache, 428033 Madrid, Spain; aguerrero@ietcc.csic.es

Resumen-- **Los residuos sólidos urbanos son uno de los problemas medioambientales más acuciantes a los que se enfrenta el mundo. Hoy en día, la incineración se considera la tecnología más eficaz para tratarlos. Sin embargo, tras el proceso de incineración, cerca del 25% de la masa total inicial de residuos son cenizas, que deben eliminarse en vertederos. Las tendencias recientes sugieren que es posible seguir avanzando en la eficiencia de los recursos convirtiendo los residuos en un recurso y cerrando así el ciclo en una economía circular. Las cenizas volantes pueden utilizarse como sustituto de los recursos naturales en la construcción, como áridos o en la fabricación de nuevos materiales. En particular, estas cenizas volantes contienen elementos como Ca, Si y Al, que permiten su utilización como materia prima para la fabricación de ligantes. En el presente trabajo, se presentarán los resultados obtenidos a partir de la caracterización fisicoquímica de las cenizas volantes. El objetivo de la investigación es explorar la viabilidad del uso de estas cenizas volantes como materia prima en la fabricación de ligantes ecológicos.**

Palabras clave— Cenizas volantes de RSU; Ligantes ecológicos; Composición química; Análisis mineralógicos; Análisis morfológicos.

Abstract— **Municipal solid waste is one of the most pressing environmental problems the world faces. Nowadays, incineration is considered to be the most effective technology for treating it. However, after the incineration process, close to 25% of the initial total mass of waste is ash, which has to be placed of in landfills. Recent trends suggest that further progress in resource efficiency is possible by turning waste into a resource and thus closing the loop in a circular economy. Fly ash can be utilized as a substitute for natural resources in construction, as in aggregates or in the manufacture of new materials. In particular, these fly ashes contain elements such as Ca, Si and Al, which make it possible for them to be used as a raw material to manufacture binders. In the present work, the results obtained from the physicochemical characterization of fly ashes will be presented. The research aims to explore the feasibility of using this fly ash as raw material in the manufacture of eco-friendly binders.**

Index Terms— MSWI fly ash; Eco-friendly binders; Chemical composition; Mineralogical analyses; Morphological analyses.

C.M. is assistant professor at Chemical and environmental Engineering at EHU. Gipuzkoa. A. M-G. is assistant professor at Thermal Engineering department from Engineering School at EHU, Gipuzkoa. I.L. is assistant professor at architecture department from engineering school at EHU, Gipuzkoa. A.G. is researcher at CSIC, Madrid.

I. INTRODUCTION

IT is estimated that about 1.3 billion tons of Municipal Solid Waste (MSW) were produced in 2012, and by 2025 the amount will increase to 2.2 billion tons (Hoornweg et al., 2012). Because of its high-volume reduction capacity and energy recovery feasibility, incineration is the most effective technology for treating MSW (Silva et al., 2019). However, municipal solid waste incineration (MSWI) generates bottom ash, fly ash (FA) and air pollution control residues (Phua et al., 2019). After the incineration process, close to 25% of the initial total mass of MSW is MSWI ash (Brunner et al., 2015), which must be disposed of in landfills. In countries where the population density is high, landfill space is limited; besides, it may pose an environmental risk if not managed properly. Recent trends suggest that further progress in resource efficiency is possible by turning waste into a resource and thus closing the loop in a circular economy. Therefore, European legislation stimulates innovation in recycling, limiting the use of landfills (D. of European Parliament, 2006). Several countries have implemented recycling initiatives to ensure that MSWI ash can be utilized as a substitute for natural resources in construction, as in aggregates, masonry blocks, roads, and so on (Goñi et al., 2011), or in the manufacture of new materials (Reijnders et al., 2007). MSWI fly ashes contain elements such as Ca, Si and Al, which make it possible for them to be used as a raw material to manufacture cements (Sarmiento et al., 2019). Nevertheless, this residue usually contains high concentrations of chloride, which can lead to critical problems if recycled as construction materials (Chen et al., 2012). In recent years, much attention has been given to hydrothermal treatments to remove chloride (Guerrero et al., 2000).

The objective in this study has been to evaluate the potential use of MSWI fly ashes from two Spanish incinerators as raw materials to manufacture eco-binders; thus, we intend to contribute to a circular economy in manufacturing industries. A physicochemical analysis of the ashes was conducted to ascertain their chemical and mineralogical composition, morphological characteristics, pozzolanic activity and textural properties. They were observed to have a high chloride content, which is counterproductive for their use in construction materials. For this reason, hydrothermal treatment was performed. The product thus obtained was also characterized. After the study, it was concluded that the treatment was appropriate for the proposed objectives, i.e., elimination of chloride and reactivation of ashes.

II. MATERIALS AND METHODS

A. Materials

The MSWI fly ash used in the study was kindly provided by two Spanish municipal solid waste incineration plants: TAR and MAT, in both cases, the ash comes from cleaning waste gases. The ashes were hydrothermally treated (HT) with a model 4522 Parr pressure reactor (Figure 1). Based on previous research experience with this type of materials (Goñi et al., 2011), hydrothermal pre-treatment was carried out under the following conditions: (I) 200 ml reactor without stirring; (II) Water as a liquid medium, using a water/solid ratio of 10/1; (III) Reactor conditions: 200 □C-1 h (HT-200 ºC-1 h) and 200 □C-4 h (HT-200 □C-4 h) (1.24 MPa pressure). At the end of the HT, the mixture was filtered, and the solid and liquid were collected separately to characterize both phases.

Fig. 1. Reactor for HT treatment.

B. Experimental methods

The chemical composition of MSWI fly ashes was determined by X-ray fluorescence (XRF). A boron glass bead was prepared with each sample of ash powder. This was done by melting in an induction microwave oven, mixing the Merck Spectro melt A12 flux (ref. no 11802) and the sample in proportions of approximately 20:1. The chemical analyses of the beads were performed in a vacuum atmosphere, using a PANalytical Axios wavelength dispersive Xray fluorescence (WDXRF) sequential spectrometer equipped with an Rh tube and three detectors (gaseous flow, scintillation and Xe sealing). Well-characterized international rock and mineral standards were used to prepare the calibration line. Further, the losson-ignition (LOI) of each sample was calculated, after subjecting an aliquot part of each sample to 1050 □C for one hour in a muffle furnace.

Quantitative analysis of the heavy metals found in MSWI fly ashes (Cr, Ni, Cu, Zn, Cd and Pb) was carried out by inductively coupled plasma-mass spectrometry (ICP-MS). Different weights of samples, acids, proportions of acids and microwave cycles were tested until a complete digestion of the ashes was achieved. Finally, digestion was optimized using 50 mg of sample, 6 ml of 65% nitric acid and 1.5 ml of hydrofluoric acid in a first microwave stage. Subsequently, these same materials were subjected to a second cycle with the addition of 15 ml of saturated boric acid (5%). The Speed wave-four microwave system (Berghof, serial number 5304000) applied a maximum of 120 □C at 80% power.

FTIR measurements were also used to characterize the MSWI fly ashes. FTIR spectroscopy was carried out with a Nicolet FTIR spectrometer using Omnic software to collect the data. The procedure for conducting FTIR spectra analysis was by KBr (potassium bromide) disk. Spectra were collected within a scanning range of 450–4000 cm-1.

The mineralogical analyses were performed by means of X-ray diffraction (XRD) using a PANalytical Xpert PRO diffractometer equipped with copper tube (meanlCuKa = 1.5418 Å, lCuKa1 = 1.5 4060 Å and lCuKa2 = 1.54439 Å), vertical goniometer (Bragg- Brentano geometry), programmable divergence crack, automatic sample exchanger, secondary graphite monochromator and PixCel detector. The measurement conditions were 40 KV and 40 mA, with a sweep of between 5 and 80 □C. The specific PANalytical Xpert HighScore software, combined with the ICDD PDF2 database, was used to process the diffractograms and to identify the phases.

Morphological and compositional analyses were performed using a Hitachi S-4800 scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDX), with a Bruker X-Flash 5030 Si-Li detector and X-Ray DX4i analyser.

C. Analysis after hydrothermal treatment.

At the end of the HT, the mixture was filtered, and the solid and liquid were collected separately. The characterization of the liquid was carried out by means of pH and conductivity. The solid was dried overnight at 50–60 □C and stored in a desiccator. A small amount of sample was taken to perform the characterization by XRD.

III. Results

Table 1 shows the chemical composition of MSWI fly ashes MAT and TAR obtained by XRF

. The main elements in both MSWI fly ashes are calcium, silica and alumina, a composition like that of the pozzolanic mineral admixture used in cementitious materials. The LOI of both MSWI fly ashes is very high, which indicates the presence of large amounts of carbonaceous materials. The high chloride content would have to be considered if the ashes were to be used as a raw material to manufacture cement. As mentioned earlier in the introduction, European legislation stimulates innovation in recycling, enhancing the outlooks for the use of waste as a secondary source of metals and other valuable chemical elements and addressing security and sustainability issues. The EC publishes a list of CRM on the basis of their relative economic importance and supply risk (European Commission, 2020). Trace elements covered in the 2020 assessment were observed by XRF, so ICP-MS analysis was also carried out. Table 2 shows the concentration of heavy metals in MSWI fly ashes compared with values from literature (Phua et al., 2019).

As can be seen, both ashes have similar results; besides, the amounts are closer to the literature's reported minimum than they are to the maximum (Phua et al., 2019).

Figure 2 shows the FTIR spectra of MAT and TAR

TABLA II
HEAVY METAL CONCENTRATIONS IN MSWI FLY ASHES (mg Kg^{-1})

Ash	Cr	Ni	Cu	Zn	Cd	Pb
MAT	165,6	92,5	679,4	5099,1	44,2	1153,5
TAR	135,8	32,5	361,2	5860,1	81,0	940,3
Lite. data (min-max)	120-2026	17-614	330-5530	3800-16800	72-456	640-5500

On the basis of the data reported in the literature (Xu et al., 2017), the main peaks are assigned as follows: at 3654 cm-1 to O-H stretching of Ca(OH)2; at 3100–3400 cm-1 to O-H symmetric and asymmetric stretching vibration of interlayer water; 2517 cm-1 vibrational mode of carbonate; 1640 cm-1 asymmetric stretching of C=O groups, possibly indicating the presence of aromatic substances or some carboxylic acids, amides and esters on the surface of the MSWI fly ashes; 1430, 872; 710 cm-1 to calcium carbonate, and 1100–1200 cm-1 to symmetric stretching vibration and asymmetric stretching of sulphate.

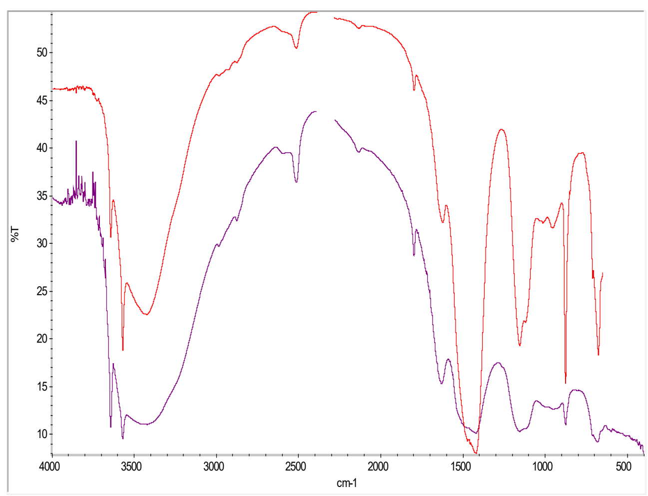


Fig. 2. FTIR spectra for MAT (purple) and TAR (red)

TABLA I
CHEMICAL COMPOSITION OF MSWI FLY ASHES (% BY WEIGHT)

Ash	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	S	Cl	LOI*
MAT	10,1	5,3	1,4	0,04	1,9	37,0	4,2	4,04	1,1	1,8	2,1	8,7	29,5
TAR	8,1	9,1	0,9	0,04	1,7	36,0	4,1	3,9	0,9	1,3	2,5	8,2	34,4

The results of the mineralogical analysis by XRD are shown in Figure 3.

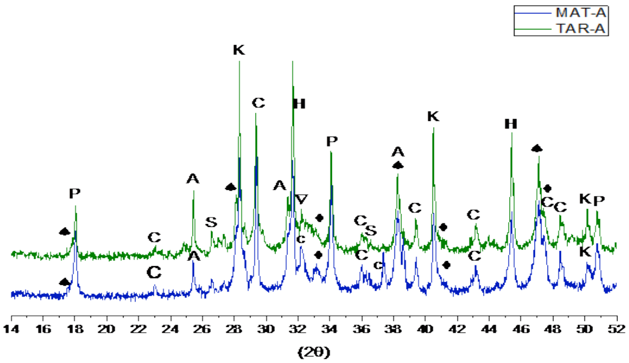


Fig. 3. DRX spectra for MAT (blue) and TAR (green)

. The major crystalline phases identified for both MSWI fly ashes are calcite CaCO3 (C), halite NaCl (H), sylvite KCl (K), anhydrite CaSO4 (A), quartz SiO2 (S), Portlandite Ca(OH)2 (P), calcium hydroxy chloride CaClOH (□), and lime phase CaO (c); once again, mineral compounds used to produce cementitious materials are observed (Yang et al., 2015). Furthermore, the presence of soluble salts made heavy metals, such as Pb and Cd, easy to release from the fly ash because of the formation of dissolved complexes like PbCl-, PbCl2, CdCl- and CdCl2 (Hu et al., 2012).

The MSWI fly ash morphology was determined by SEM (Figure 4). The images on the left belong to MAT and the images on the right to TAR, the images were obtained at 800x magnification. Different numbers can be seen on the images, which show the points where EDX analyses were conducted (Figure 5).

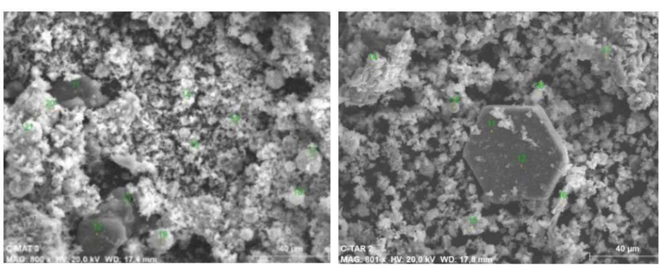


Fig. 4. SEM images of MSWI fly ash: (left) MAT; (right) TAR. The green numbers show the points where EDS analyses were conducted (results in Figure 5)

Images show a general view of both ashes. Both present a poorly defined microstructure with a particulate matrix. The fly ash particles are revealed as spherical granules with small particles adsorbed on the surface. The particles are smaller and less compacted in the case of TAR. Larger-sized crystals than the particles are dispersed in this particulate matrix. Cenospheres are also observed, dispersed through the particulate matrix. Worthy of note is that more cenospheres are found in TAR. The MSWI fly ashes are morphologically like MSWI fly ashes found in the literature (Yu et al., 2020).

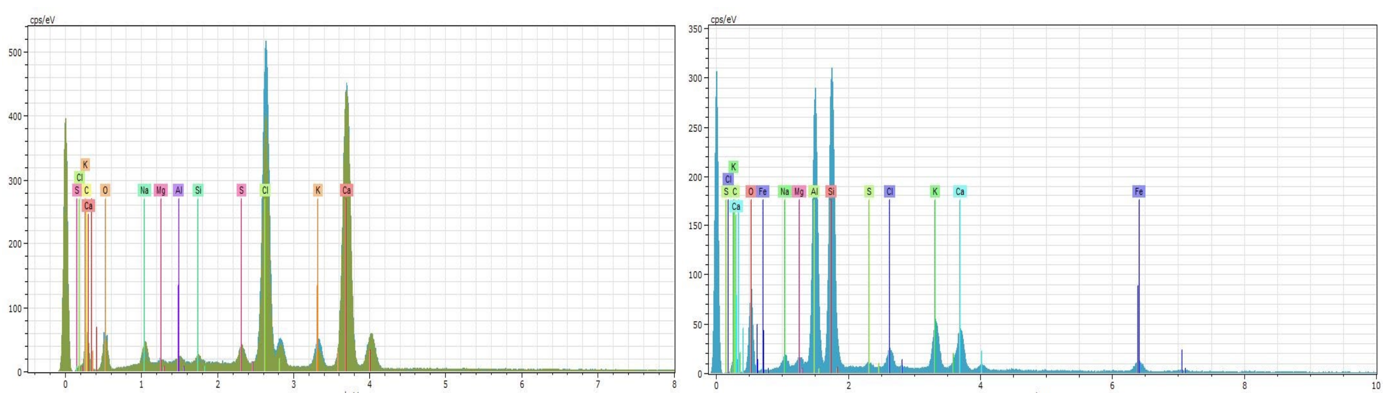
A. Analysis after hydrothermal treatment

After HT the pH stabilized at about 12.1, and conductivity, at 40 mS/cm. Further, it was observed that a plateau of stabilization was reached after one hour of treatment for pH and conductivity, which indicates that it is not necessary to perform HT for more than one hour. The solid after HT was also analysed. The first measurement was the amount of chloride by XRF, which was 3.318% for MAT and 3.041% for TAR. In both cases, 62% of chlorines are eliminated after HT.

IV. CONCLUSIONS

Municipal solid waste incineration fly ashes from two Spanish cities have been characterized to analyse the possibilities of their use as raw material in the manufacture of eco-friendly binders. The following conclusions can be drawn from the results:

- The main elements in MSWI fly ashes are calcium, silica, alumina and iron, a composition like that of the common mineral admixture used in cement-based materials.
- Chemical analysis has shown large amounts of chloride and traces of other contaminants, which mean the ashes must be pre-treated before they can be used as raw material in eco-friendly binders' production. Hydrothermal treatment (HT-200 □C-1 h) is a useful way to dissolve part of the chloride.
- Both ashes show a microparticulate morphology with crystals and cenospheres.
- Most of the chloride is found in the microparticulate matrix, which facilitates its leaching during the hydrothermal pre-treatment.



MAT TAR

Fig. 5. EDS analyses of MSWI fly ash: MAT (green); TAR (blue).

ACKNOWLEDGEMENTS

The authors would like to thank the Diputación Foral de Gipuzkoa (82/17) and the University of the Basque Country, UPV/EHU (PPG17/22), for financially supporting this work.

REFERENCES

P.H. Brunner, H. Rechberger, Waste to energy – key element for sustainable waste management, Waste Manage. 37 (2015) 3–12. https://doi.org/10.1016/j.

W.S. Chen, F.C. Chang, Y.H. Shen, M.S. Tsai, C.H. Ko, Removal of chloride from MSWI fly ash, J. Hazard. Mater. 237 (2012) 116–120. https://doi.org/10.1016/j.jhazmat.2012.08.010.

DIRECTIVE OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL amending Directives 2008/98/EC on waste, 94/62/EC on packaging and packaging waste, 1999/31/EC on the landfill of waste, 2000/53/EC on end-of-life vehicles, 2006/66/EC on batteries and accumulators and waste batteries and accumulators, and 2012/19/EU on waste electrical and electronic equipment/* COM/2014/0397 final - 2014/0201 (COD) */. https://eur-lex.europa.eu/legal-content/EN/TXT/? uri=CELEX:52014PC0397.

European Commission, 2020. Study on the EU's list of Critical Raw Materials. file:///C:/Users/iabmagoc/AppData/Local/Temp/CRM%20list%202020_Final%20Report.pdf.

S. Goñi, A. Guerrero, A. Macías, M.P. Lorenzo, Materias primas alternativas para la fabricación de cementos más ecoeficientes de baja energía, Revista ALCONPAT. 1, (2011) 17–29. https://doi.org/10.21041/ra.v1i1.3.

A. Guerrero, E. Fernandez, A. Macias, S. Goñi, Hydrothermal treatment of fly ash from municipal solid waste incineration, in Waste Materials in Construction WASCON 2000, Elsevier Science Ltd.

D. Hoornweg, P. Bhada-Tata, What a Waste: A Global Review of Solid Waste Managament, Urbal Development Series Knowledge Papers. (2012) 151–198. http://hdl.handle.net/10986/17388.

Y. Hu, P. Zhang, D. Chen, B. Zhou, J. Li, X. Li, Hydrothermal treatment of municipal solid waste incineration fly ash for dioxin decomposition, J. Hazard. Mater. 207 (2012) 79-85. https://doi.org/10.1016/j.jhazmat.2011.05.068.

Z. Phua, A. Giannis, Z.L. Dong, G. Lisak, W.J. Ng, Characteristics of incineration ash for sustainable treatment and reutilization, Environ. Sci. Pollut. 26 (2019) 16974–16997. https://doi.org/10.1007/s.11356-019-05217-8.

I. Reijnders, The cement industry as a scavenger in industrial ecology and the management of hazardous substances, J. Ind. Ecol. 11 (2007) 15–25. https://doi.org/10.1162/jiec.2007.997.

L.M. Sarmiento, K.A. Clavier, J.M. Paris, C.C. Ferraro, T.G. Townsend, Critical examination of recycled municipal solid waste incineration ash as a mineral source for Portland cement manufacture-A case study, Resour Conserv Recycl. 148 (2019) 1–10. https://doi.org/10.1016/j.resconrec.2019.05.002

R.V. Silva, J. Brito, C.J. Lynn, R.K. Dhir, Environmental impacts of the use of bottom ashes from municipal solid waste incineration: A review, Resour Conserv Recycl. 40 (2019) 23–35. https://doi.org/10.1016/j.resconrec.2018.09.011.

Y. Xu, Y. Fu, W. Xia, D. Zhang, D. An, G. Quian, Municipal solid waste incineration (MSWI) fly ash washing pretreatment by biochemical effluent of landfill leachate substitute for water, Environ. Technol. 39 (15) (2017) 1949–1954. https://doi.org/10.1080/09593330.2017.1345985.

K.H. Yang, Y.B. Jung, M.S. Cho, S.H. Tae, Effect of supplementary cementitious materials on reduction of CO2 emissions from concrete, J. Clean. Prod. 103 (2015) 774-783. http://dx.doi.org/10.1016/j.jclepro.2014.03.018.

X. Yu, J. Jiang, Phosphate microbial mineralization consolidation of waste incineration fly ash and removal of lead ions, Ecotoxicol. Environ. Saf. 191 (2020) 110224, https://doi.org/10.1016/j.ecoenv.2020.110224.

Reconocimiento – NoComercial (by-nc): Se permite la generación de obras derivadas siempre que no se haga un uso comercial. Tampoco se puede utilizar la obra original con finalidades comerciales.