Technological behaviour of ceramic tile bodies obtained by recycling of copper slag and MSW fly ash wastes

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ABSTRACT

The aim of this research has been to evaluate the feasibility of adding this residue in manufacturing of ceramic bricks, as well as tested the immobilization of Pb and As in ceramic tiles. The results showed the viability of replacing up to 40% of clay with these residues, with an improvement in the resistance of pieces compared to ceramics made without adding residues. The immobilization of As and Pb was also observed in the ceramic bodies obtained. Leaching tests have showed that immobilization of both elements (As and Pb) improves with increasing of the firing temperature. Regarding the lead and arsenic contents, all ceramic tiles here investigated comply with the limits established by the ministerial order for their deposit in non-hazardous waste landfills. The leaching values of metals into the environment during the useful lives of these ceramic materials (bricks) were over an order of magnitude lower than the threshold and complied by the Standards Rules for environmental protection.

Weight (%)	Ceramic clay
SiO_2	51.39
Al_2O_3	14.85
Fe_2O_3	6.95
CaO	15.29
MgO	2.95
Na_2O	0.383
K_2O	4.22
TiO_2	0.940
MnO	0.050
P_2O_5	0.215
Total SO_3	0.620
O.M. 500ºC	2.00
Deads (1000ºC)	13.20
$CaCO_3$	24.00
SO_4^{-2} (solubles)	4240 (ppm)
Cl^- (solubles)	199.90 (ppm)

Chemical composition of the standard ceramic clay

%	Cu-Slag	%	Cu-Slag
SiO_2	50.17	CuO	0.82
Fe_2O_3	17.14	SO_3	0.16
CaO	15.33	Al_2O_3	8.92
MgO	1.03	TiO_2	0.41
K_2O	2.20	MnO	1.05
P_2O_5	0.15	LOI	-1.67

Parameter	Units	MSW fly ash
O.M. 500ºC	%	42.60
LOI (1000ºC)	%	69.98
$CaCO_3$	%	7,86
SO_4^{-2} (solubles)	ppm	9048
Cl^- (solubles)	ppm	849.1
SiO_2	%	10.53
Al_2O_3	%	4.35
Fe	mg/kg d.m.	9800
Ca	mg/kg d.m.	60
Mg	mg/kg d.m	45
Na	mg/kg d.m	1012
K	mg/kg d.m	2113
Mn	mg/kg d.m	177
P	mg/kg d.m	28,36
Total SO_3	%	5,95

Chemical composition of MSW fly ashes

Heavy metals	MSW (mg/kg)
Cu	89
Zn	176
Pb	51
Hg	0.15
As	0.22
Cd	3.38

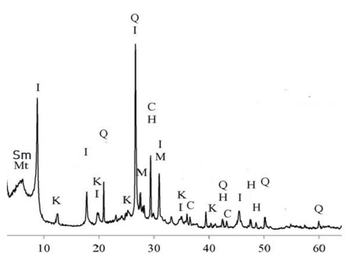
Heavy metals	Cu-Slag (%)
Zn	0.29
Co_3O_4	0.07
PbO	0.41
As_2O_3	0.59

Heavy metals content (mg/kg dry matter)

Chemical composition of Cu-slag residue

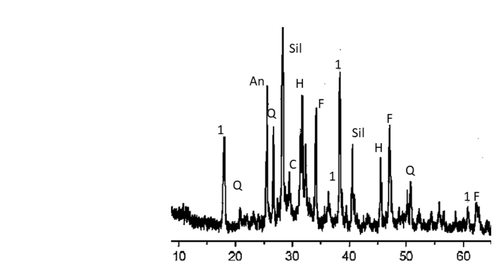
Firing temperature 900 °C Added Residues (%)	As	Pb
0	0.3 ± 0.06	0.07 ± 0.01
16	0.60± 0.03	0.10± 0.01
22	0.72± 0.01	0.44± 0.02
28	0.80 ± 0.02	0.64± 0.03
34	1.1± 0.03	0.74± 0.01
40	1.2 ± 0.04	0.80± 0.03
Firing temperature 950 °C Added Residues (%)	**As**	**Pb**
0	0.22 ± 0.06	0.07 ± 0.01
16	0.34± 0.03	0.08± 0.02
22	0.52± 0.01	0.31± 0.02
28	0.60 ± 0.02	0.54± 0.03
34	0.8± 0.03	0.65± 0.02
40	0.9 ± 0.04	0.70± 0.03
Firing temperature 1000 °C Added Residues (%)	**As**	**Pb**
0	0.10 ± 0.01	< 0.05
16	0.16± 0.03	< 0.05
22	0.22± 0.01	< 0.05
28	0.32 ± 0.01	< 0.05
34	0.40± 0.02	< 0.05
40	0.48 ± 0.04	< 0.05
Firing temperature 1050 °C Added Residues (%)	**As**	**Pb**
0	0.05 ± 0.02	< 0.05
16	0.10± 0.03	< 0.05
22	0.12± 0.01	< 0.05
28	0.18 ± 0.02	< 0.05
34	0.22± 0.02	< 0.05
40	0.38 ± 0.03	< 0.05
Landfill for inert wastes	0.5	0.5
Landfill for non-hazardous wastes	0.2	10

RESULTS AND DISCUSSION



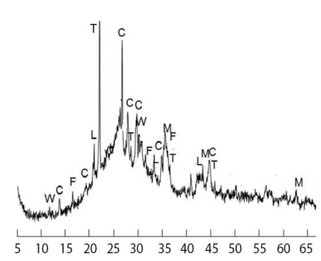
Clay

Legend: Sm-Mt: smectite-montmorillonite; I: illite; k: kaolinite; Q: quartz; H: hematite; M:microcline; C: calcite



MSW fly ash

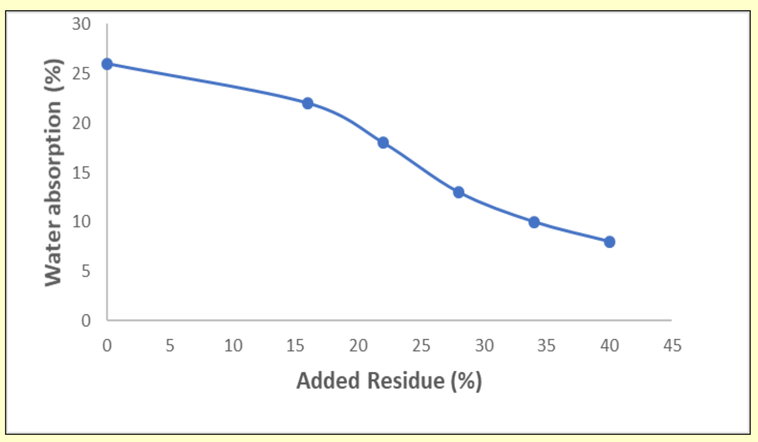
Legend: 1: CaClOH; Q: quartz; An: anhydrite; Sil: silvine; H: halite; F: fluorite; C: calcite.

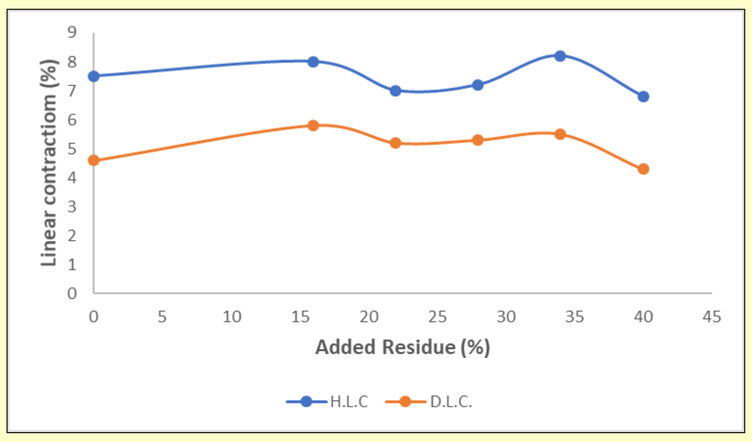


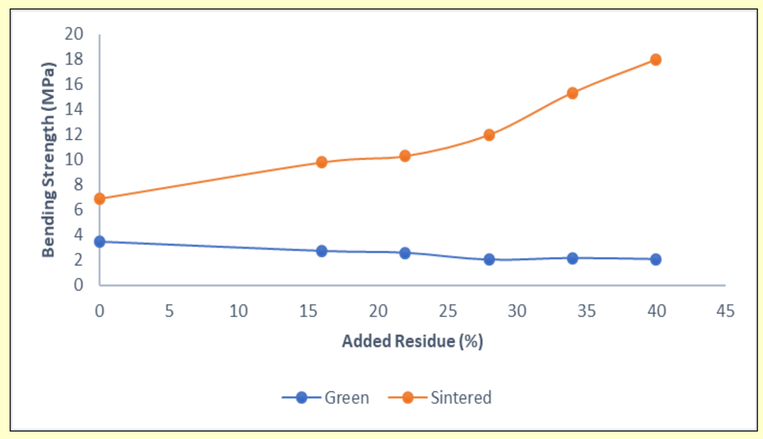
Cu-Slag

Legend: W: wollastonite; C: clinoferrosillite; F: fayalite; L: microcline;T: cristobalite; M:magnetite.

The minerals present in the selected clay were illite, kaolinite, and chlorite, with quartz and small quantities of hematite, feldspar, calcite and dolomite. The mineral phases present in the MSW fly ash were quartz (SiO_2), anhydrite ($CaSO_4$), silvine (KCl), halite (NaCl), fluorite ($Ca(OH)_2$) and CaClOH. The Cu-slag is mainly made up of cristobalite (SiO_2), clinoferrosillite ($FeSiO_3$) and to a lesser extent by magnetite (Fe_2O_4) and fayalite (Fe_2SiO_4).







The Standards Properties for construction bricks limit the water absorption at a maximum value of 13%. The addition of waste makes it possible to produce structural masonry bricks, which was not possible by using only the clay raw material here analyzed. By using only this clay raw material, it is only possible to manufacture non-structural ceramics which less exigences such as higher WAC and/or roof tiles.

CONCLUSION

The main advantages of the introduction of copper slag jointly with low percentages of MSW fly ashes in the production of tiles and bricks are: a) The recycling of wastes whose generation is increasing every year; b) the immobilization of dangerous elements contained in these residues, mainly copper slag and c) the improvement of technological properties of ceramic tile bodies obtained.

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