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Lab Scale Granulation Tests of Artificial Aggregate Production from Marine Sediments and Industrial Wastes

Luca Di Palma, Daniele Mancini, Franco Medici*

Dipartimento di Ingegneria Chimica Materiali Ambiente, “Sapienza” Università di Roma,
via Eudossiana 18, 00184 Roma (Italy).
franco.medici@uniroma1.it

Preliminary experimental results on the solification/stabilzation of dredged marine sediments (MS) and the non-metallic fraction of automotive shredder residues (NMASR) with coal fly ashes (CFA) are reported. Lab scale experiments of wet granulation at room temperature of these wastes are presented and discussed: cement was used as a binder, while water addition was dosed to optimize granules amount and size.
The obtained granules were then subjected to standard leaching tests according to Italian regulation. The results of the leaching tests showed, for all the experimented wastes, a good level of stabilization: heavy metals and ions content was within the limits provided by Italian regulation for landfill disposal as not dangerous waste, while a COD content exceeding the above mentioned limit was detected. This was attributed to plastics and an organic contamination by vehicles fluids in the case of NMASR, and to sulphides and iron content in the case of marine sediments.

1. Introduction

The main effort in the future, according to the European directives on wastes, will be devoted to limit hazardous wastes disposal into landfill to only stabilized or incinerated wastes. To this aim, in a near future a huge amount of industrial wastes must be treated utilizing different technologies (Keyvani, 2002), to reduce their volume and potential toxicity (Jantzen et al., 2001).
The experimental assessment and the development of new and cheaper technologies for the recycling and reusing of several waste fractions will be therefore of a growing interest both from an economical and ecological point of view. At this purpose three different types of hazardous wastes were selected and tested (coal fly ashes, CFA, the inorganic non metallic fraction of the automotive shredding residues, NMASR, and marine sediments, MS).
Harbour basin and waterways have to be dredged in order to maintain an adequate shipping channel depth. The collected sediment is de-watered in drainage pounds and the residue is generally reused.
Harbour sediments are often rich in heavy metals: since they are not subjected to degradation phenomena, they can easily be suspended or dissolved by surface waters and so the need exist to perform experimental tests aiming at sediment remediation.
Among the most common industrial wastes, fly ashes from coal thermoelectric plant have a great environmental impact because of the large amount of their production (38 Mt/y in EU in the year 2011, Bech and Feuerborn, 2011). Their reuse and recycling could be practically complete in cement (Lam et al., 2010) or concrete mixtures (Rostami et al., 2009), due to the pozzolanic behaviour of fly ashes. As a result, in Italy, cement and concrete industry may easily absorb the whole production of these ashes.

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Every year in EU nations about 12 M vehicles are shredded (Pera et al., 2004); utilizing specific treatment methods, 75 % of components of the vehicles can be recycled, while the remaining part, named ASR, automotive shredding residue, constitutes a multi component waste that require an appropriate disposal. In UE around 3 Mt of ASR were generated in the year 2011 (Vermeulen et al., 2011): about 50 % of ASR is composed by rubber, glass or plastics, which can be either transformed into alternative fuel or recycled, while the remaining fraction is incombustible and it has not yet been valorised, but generally, after a non-ferrous metal recovery, landfilled as ASR residue. This method of discharge induces problems of disposal, and when such waste is not properly chemically stabilized may produce pollution in soils.
Authors think that a cheap and efficient method to reuse those incombustible wastes is chemical stabilization by means of wet granulation at room temperature. This process involves the immobilization of raw fluff in granules produced by mixing selected amount of fluff with a binder in the presence of other additives in a rotating device.
Therefore, the aim of this paper was to optimise the granules production from those two widely produced wastes, and to investigate the physical and mechanical behaviour of stabilized products with the final goal to produce a lightweight aggregate, that may be utilized in concrete industry (Sagoe-Crentsil et al., 2001; Sani et al., 2005).

2. Materials and methods

2.1 Materials

Experimental tests were performed on the non metallic automotive shredding residue produced in the shredding plant Italferro at S. Palomba (Roma, Italy), and on marine sediments collected at several depth in an Italian harbour. Table 1 shows the chemical composition and the heavy metals contents of the selected materials.

Table 1: Chemical composition (oxides) and heavy metal contents of selected materials

Component	CFA (%w)	NMASR (%w)	MS (%w)	Component	CFA (mg/kg)	NMASR (mg/kg)	MS (mg/kg)
SiO_2	46.5	28.8	63	Cadmium	5	11	< 1
Al_2O_3	24.4	5.3	11	Chromium	38	< 2	32
Fe_2O_3	10.1	25.6	8.3	Copper	24	3727	50
CaO	7.0	8.1	1.8	Lead	18	7420	27
MgO	1.1	2.9	0.9	Zinc	45	450	65
Na_2O+K_2O	1.8	2.7	2.5	Residue 105 °C (%w)	94	91.1	68.9
LOI (1100 °C)	5.2	14.0	9.6	Residue 600 °C (%w)	-	39.4	-

2.2 Experimental procedures

The aim of the experiments was to set up a process to produce aggregate for concrete utilizing the two previously mentioned wastes. The proposed process deals with three steps: the selection of the product, the granulation and the preparation of concrete samples. This paper was focused on the first and, mainly, the second step, while the results of the third one have been reported elsewhere (Alunno Rossetti et al., 2011)
The first step of the experimentation aimed at selecting a fraction characterized by a negligible heat of combustion and a grading range to be suitable to be granulated in the subsequent phase. As regards the NMASR, this step was performed directly in the shredding plant. The residue of the shredder was subjected to metal recovery in two step: iron was first recovered by magnetic treatment, while the remaining fraction was sieved and the passing through a 12 mm sieve was collected.
Basing on the assumption that the contaminants are mainly concentrated in the pelitic fraction, for marine sediments, only the fraction passing a 2 mm sieve was considered.
Lab scale granulation tests of the selected fraction were performed using the granulator device shown in Figure 1 and designed to the purpose. Each test was performed using a total amount of mixture of 1-2 kg. In lab scale granulation tests cement CEM II-A/LL 42.5 (C) and fly ashes (silico-aluminated

product, CFA) produce in a thermoelectric plant located in Brindisi (Italy) were used as binder. Three series of tests were carried out: in the tests F1 and F2 the NMASR was granulated, while in the test S, marine sediments were granulated. In the test F2, in order to evaluate the effect of water reduction during mixing, a commercial superplasticizer (Basf ACE 363) was utilized.

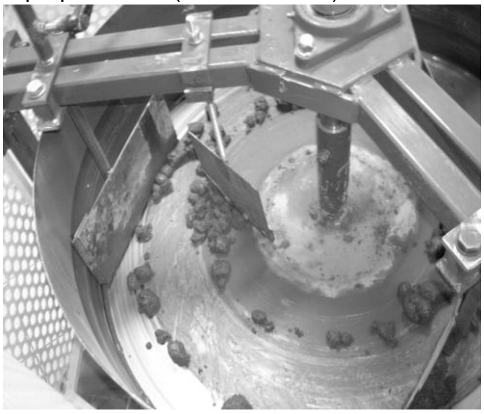

Figure 1: Granulation tank

The influence of the water content (W) and of the fly ash/residue (CFA/R, where R was NMASR or MS) ratio on the range of granulation and on granules diameter was evaluated. The experimental conditions of the tests are summarized in Table 2.

Table 2: Experimental conditions in the granulation

Test	W/C	CFA/R	W/C+CFA
F1	1	1	0.375
F2	0.92	0.83	0.367
S	1	1	0.6

Water dosage was the operating parameter: depending on the operative condition of wet granulation, water dosage was varied to individuate a range from a minimum necessary to obtain the granules, to a maximum preventing the formation of a semifluid sludge in the granulator: this value was considered as the optimal value for the granulation process (Alunno Rossetti et al, 2006).

2.3 Leaching test

After a 28 days period of curing, at room temperature, in moisture saturated chamber, the obtained granules were sieved into three granulometric fractions (< 4mm, between 4 and 12.5 mm, and >12.5 mm) and subjected to a leaching tests, according to the UNI EN 12457-2 (one stage batch test at a liquid to solid ratio of 10 L/kg with particle size below 4 mm) and UNI EN 12457-4 (one stage batch test at a liquid to solid ratio of 10 lLkg with particle size below 10 mm) (UNI EN 12457, 2004).

The pH of the leached solutions was measured with a Crison GP42 pH meter; a ionic chromatograph Dionex DX-120 was used to determine ionic species; a Philips PU 9200 atomic absorption spectrophotometer was used to determine the metal content. Total organic carbon (TOC) was determined using a Shimadzu TOC 5000-A Analyzer (5 % standard deviation) as the difference between total carbon content (TC) and inorganic carbon amount (IC). Chemical oxygen demand (COD) was determined utilizing a standard ASTM method (D1256-6 Dichromate Oxygen Demand). The aim of the experiments was to set up a process to produce aggregate for concrete utilizing the two previously mentioned wastes.

3. Results and discussion

3.1 Granulation tests

Lab scale tests results confirmed the effectiveness of the granulation process. The amount of the granules produced and the size distribution obtained in the tests performed in the pilot scale granulator was strongly dependent upon the nature of the material used, as shown in Table 3.

Table 3: Experimental results of the granulation tests

Test	% granulated	<4 mm	4 mm to 12.5 mm	> 12.5 mm
F1	100	48	44	8
F2	100	42	36	22
S	100	56	29	15

Results show that for all the investigated wastes, an almost total granulation was achieved, though the distribution of granules among the three considered fractions was quite different. The granules produced from marine sediments were, in fact, mainly distributed in the finest fraction, while, in the case of NMASR, low size granules were obtained in the absence of the superplasticizer, according to the water reduction properties of the product used. The size distribution of the produced granules allows to consider marine sediments more promising to produce fine aggregates with respect to NMASR, that also appeared to have a lower granulation range (i.e. increasing water content, the size of granules increased faster).

As regards the physical and mechanical properties of the produced granules, depending upon the composition of the mixture, the specific weight of the granules varies in both cases between 1400 and 2000 kg/m^3, originating a family of lightweight aggregates. The compressive strength values of the granules varied in the range between 0.8 and 1.5 MPa, and, as expected, was higher when a lower water amount was used.

3.2 Leaching tests

The results of leaching tests are reported in Tables 4 and 5.

Table 4: Results of the leaching tests: chemical characterization and organics.

	pH	K (mS)	TC (mg/L)	IC (mg/L)	TOC (mg/L)	COD (mg/L O_2)
F1						
<4 mm	7.30±0.10	0.58±0.03	144.0	3.6	140.6	354±37
4-12.5 mm	8.54±0.40	0.48±0.02	84.3	21.0	73.3	193±24
>12.5 mm	7.21±0.12	0.63±0.05	119.4	29.4	90.0	235±40
F2						
<4 mm	7.86±0.15	0.55±0.04	179.4	4.8	174.2	375±28
4-12.5 mm	7.49±0.10	0.53±0.05	100.2	14.2	86.0	140±15
>12.5 mm	7.38±0.15	0.71±0.06	162.0	15.2	146.8	338±30
S						
<4mm	7.81±0.40	2.51±0.05	15.7	9.1	6.6	93±10
4-12.5 mm	7.40±0.25	2.34±0.06	16.1	11.4	4.7	51±10
>12.5 mm	6.86±0.05	3.05±0.06	20.2	9.7	10.5	123±12

The results of leaching tests, compared to those of the raw material (Table 1), allows to assess that a first strong immobilizing action with respect to heavy metals and organics was associated to the formation of the granules, with the only exception of a high COD content. The limit imposed for COD by Italian regulation (Italian Environmental Regulation, 2010) for landfill disposal of hazardous waste is, in fact, 100 mg/L. In the case of the granules obtained from NMASR, as already observed in other

studies (Alunno Rossetti et al., 2011), the high COD values could be due to both the presence of plastic residues in the sieved fraction, and to a slight contamination by the fluids contained in vehicles tanks. In the case of the granules produced from marine sediments, the measured COD was mainly attributed to the release of oxidizable compounds such as sulphides and iron containing species, as confirmed by the low the low organic content of the sediments, as resulted by the TOC values in the eluates.
This assumption was confirmed by the COD/TOC ratio values: in fact, in the tests F1 and F2 that ratio was in the range between 2 and 2.6, while for the granules obtained from marine sediments it was in the range between 12 and 14.1.

Table 5: Results of the leaching tests: ions (average standard deviation < 5 %).

	Cl^- (mg/L)	F^- (mg/L)	SO_4^{2-} (mg/L)	Ca^{2+} (mg/L)	Cd (mg/l)	Cu (mg/l)	Pb (mg/l)	Zn (mg/l)
F1								
<4 mm	9.71	4.71	42	26.2	<0.1	0.39	0.1	0.42
4-12.5 mm	10.13	0.82	58.4	21.7	<0.1	0.37	<0.1	0.31
>12.5 mm	20.47	0.69	90.9	10.4	<0.1	0.46	0.1	0.41
F2								
<4 mm	5.84	4.07	34.2	17.5	<0.1	0.26	<0.1	0.2
4-12.5 mm	2.73	1.24	14.6	23.8	<0.1	0.16	<0.1	0.12
>12.5 mm	12.81	6.51	125.3	9.7	<0.1	0.4	0.15	0.2
S								
<4 mm	170.47	0.8	207.6	184.9	<0.1	<0.1	<0.1	0.1
4-12.5 mm	549.59	0.61	463	138.2	<0.1	<0.1	<0.1	0.16
>12.5 mm	778.32	0.34	860.9	205.3	<0.1	<0.1	<0.1	0.16

In addition, results show that the pH of the eluted solutions was found to be only slightly dependent on both the granules nature and diameter. The conductivity values resulted correlated with the release of chlorides and sulphates, and were particularly high for marine sediments. The release of fluorides, bromides and nitrates was negligible in all the tests.
As regards the release of metallic elements, all the granules showed a good level of stabilization (Table 5): they are all within the limits provided by Italian regulation for landfill disposal as not dangerous waste (Italian Environmental Regulation, 2010).
The obtained results allow us to evaluate the cumulative amount of released substances and not to evaluate the leaching kinetics. To this purpose, a dynamic leaching tests should be utilized, but the aim of the present work was only to verify whether the stabilized product could be reused.

4. Conclusions

In this paper pilot scale immobilization tests of the non metallic fraction of automotive shredding residue, or marine sediments by wet granulation in cementitious matrix were performed. The obtained granules showed mechanical and physical properties suitable to be used as artificial aggregates in concrete mixes. The results of leaching tests performed according to the European Standards showed in both cases a good chemical fixation with respect the main pollutants, with the main exception of organic compounds (as COD). This does not allow the direct reuse of granules, but their use as artificial aggregate in concrete mixes appears to be promising.

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