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Valorization of automotive shredder residue in building materials

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Abstract

Every year in EU nations, it is estimated that 3 million tonnes of automotive shredder residue (ASR) are generated. Half of the ASR is composed of rubber, textiles and plastics, which can be either transformed into alternative fuel or recycled. The second half, which is landfilled, is incombustible and has not yet been valorized.

This waste contains 30% organic matter, as well as inorganic compounds such as quartz, calcite, magnetite, hematite, and anhydrite. It is also very rich in zinc (1–3.5%) and lead (0.7–3.3%). These elements are powerful retarders of ordinary Portland cement. For this reason, two ways of processing of this waste have been investigated: (1) transformation into aggregates after a thermal treatment followed by a chemical treatment or (2) directly into concrete with the use of calcium sulfoaluminate cement.

This second way is especially very interesting for engineers and scientists. As established by leaching tests, zinc and lead are integrated and fixed in the structure of ettringite, the main hydration product of calcium sulfoaluminate cement. Therefore, it is possible to produce concrete for some applications including road construction from this currently landfilled "waste" (i.e., the ASR is shown to be useful recyclable material that can be converted into an environmentally friendly "green" concrete).

Keywords: Grinding; Thermal treatment; Hydration products; Compressive strength; Waste management

1. Introduction

Every year in EU nations, 12 million cars turn to end-of-life vehicles (ELVs). In the treatment methods of ELVs, shredders recycle 75% of the vehicle: 70% iron and steel and 5% nonferrous metals. The remaining shredder fluff, called automotive shredder residue (ASR), represents 25% by mass per vehicle and is landfilled. Household fittings (washing machines, refrigerators, and other "white" machines) may be shredded along with discarded cars. About 3 million tonnes of ASR are landfilled every year in Europe. ASR may be separated into two categories equal in mass, according to combustibility criteria. The first half, composed of rubber, textiles, and plastics may be either transformed into alternative fuel [1–3] or used in the plastics industry as demonstrated by the Argonne National Laboratory (www.es.anl.gov). The second half, called incombustible shredder residue (ISR), has not yet been valorized.

ISR contains 30% organic matter, as well as inorganic compounds such as quartz, calcite, magnetite, hematite, and gypsum. It is also very rich in zinc (1–3.5%) and lead (0.7–3.3%). These elements are powerful retarders of ordinary Portland cement. Two ways of valorization have, therefore, been investigated:

(1) ISR was calcined at 700 °C to eliminate organic matter and then immersed in sodium hydroxide solution to transform metals and oxides into metallic hydroxides, or in sulfuric acid to transform metals and oxides into metallic sulfates. After such treatment, ISR was washed and dried before its introduction in mortar cast with ordinary Portland cement.
(2) ISR was directly mixed with calcium sulfoaluminate cement to prepare concrete for road construction. The results obtained show, from an environmental point of view, that this solution is more promising. Heavy metals are bound in the concrete matrix and immobilized, thus avoiding any treatment.

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2. Transformation of ISR into aggregates compatible with ordinary Portland cement

2.1. Characterization of ISR

Two samples of ISR were investigated. Their chemical composition is shown in Table 1.

The maximum diameter of the particle size distribution was 4 mm.

The quantity of aluminum in metallic form has not been assessed.

2.2. Thermal treatment

ISR was treated for 5 h in an electrical fixed-bed furnace equipped with a gas extraction system. Four-kilogram batches were prepared. After cooling to ambient temperature, treated ISR was separated into three grain-size classes: < 100, 100–500, and >500 μm. Iron was extracted from particles larger than 500 μm. The results obtained are presented in Tables 2–4.

As shown in Table 4, the porosity and water absorption of thermally treated aggregates were high, and the specific gravity was lower than that of usual natural aggregate.

The mineralogy of aggregates was assessed by X-ray diffraction; the results obtained are shown in Table 5. The main components are quartz, calcite, magnetite, and hematite.

2.3. Behavior of thermally treated ISR

The fraction larger than 500 μm was used as sand in standard mortar prepared with OPC CEM I 52.5 (European standard EN 197). The OPC-to-sand ratio was 1:3. The quantity of water was adjusted to get the same workability as that presented by mortar cast with standard sand. The setting time was measured for each composition, using the Vicat's needle, as shown in Table 6.

The use of thermally treated ISR drastically increased the setting time of mortar. In addition, for ISR 2, a gaseous emission (hydrogen) occurred after casting, due to the reaction between OPC and aluminum contained in ASR. Such aggregates cannot be directly used in concrete. With other fractions (< 100, 100–500 μm) of ISR, delay in setting was further increased.

Table 1
Chemical composition of ISR (oxides)

Element (%)	ISR 1	ISR 2
SiO_2	28.78	30.68
Al_2O_3	5.32	4.57
Fe_2O_3	25.57	21.34
MnO	0.24	0.22
MgO	2.92	3.53
CaO	8.11	9.34
Na_2O	2.08	2.85
K_2O	0.63	0.50
TiO_2	0.55	0.54
P_2O_5	0.95	1.38
LOI	14.04	12.08
C_{org}	4.98	4.82
Cl	0.18	0.22
S_{tot}	0.48	0.31
Ba	0.48	0.49
Cr	0.70	0.55
Cu	1.69	2.75
Ni	0.32	0.32
Pb	3.30	3.34
Zn	2.50	2.21

Table 2
Characterization of ISR treated at 700 °C

Sample	Organics (%)	Metallic particles (%)	Incombustible (%)
ISR 1	14	7	79
ISR 2	28	17	55

2.4. Chemical treatment of calcined ISR

Three types of chemical treatments have been investigated:

1. Immersion of thermally treated ISR in sodium hydroxide solution (5 M) to transform metals and metallic oxides into metallic hydroxides;
2. Immersion of thermally treated ISR in a solution of sulfuric acid (10%) to transform metals and metallic oxides into metallic sulfates; and
3. Immersion in sodium hydroxide solution, washing, and immersion in sulfuric acid.

After 8 h of immersion, ISR was washed, passed through a 100-μm sieve and dried at 70 °C. The whole fraction (100 μm to 4 mm) was therefore used as sand in mortar.

Three types of sand were prepared and compared to a plain silicocalcareous sand (S0):

−S1: 100% chemically treated ISR
−S2: 50% chemically treated ISR + 50% S0
−S3: 30% chemically treated ISR + 70% S0

Standard mortar (OPC/S = 1:3) was prepared with these different sands. The w/c was adjusted to get the same workability (150 mm flow) (Table 7). The initial setting

Table 3
Particle size distribution of ISR treated at 700 °C (incombustible fraction)

Fraction (%)	ISR 1	ISR 2
< 100 μm	18	23
100–500 μm	29	49
>500 μm	53	28

Table 4
Physical properties of aggregates >500 μm

Property	ISR 1	ISR 2
Specific gravity	2.11	2.12
Water absorption (%)	14.80	14.10
Porosity (%)	15.40	16.12

time and compressive strength of these mortars are shown in Figs. 1 and 2.

The w/c of mortars prepared with treated ISR was always higher than that of control mortar prepared with S0 (w/c = 0.5) due to the higher porosity of aggregates.

The initial time of setting of mortars was always higher than that of control mortar (330 min).

The 28-day compressive strength reached by the control mortar was 51.2 MPa. The use of ISR 1 generally led to higher strength than ISR 2. S2 and S3 for ISR1 presented very good strength, especially when the combined treatment ($NaOH + H_2SO_4$) was used. From these results, it can be concluded that chemically treated ISR can be used as partial replacement of sand in concrete at least at a level of 50%.

2.5. Environmental considerations

During heat treatment (thermogravimetric analysis up to 700 °C at a temperature rate of 4 °C/min), gaseous emissions were analyzed by mass spectrometry. Emitted gases were water vapor, CO_2, aromatics (benzene, toluene), and some halogen by-products. The risk of dioxin emission existed and emissions had to be carefully treated by an industrial process.

3. Immobilization of ISR in calcium sulfoaluminate cement

3.1. Fixation of heavy metals by calcium sulfoaluminate cement (CSA)

Sulfobelite cements, also called sulfoaluminate–belite cements, contain the phases belite (C_2S) and yeelimite, or tetracalcium trialuminate sulfate ($C_4A_3\bar{S}$), and gypsum ($C\bar{S}H_2$) as their main constituents. When CSA cement hydrates, ettringite ($C_6A\bar{S}_3H_{32}$) is formed according to the following reactions [4]:

$$C_4A_3\bar{S} + 2C\bar{S}H_2 + 36H \rightarrow C_6A\bar{S}_3H_{32} + 2AH_3$$

in the absence of calcium hydroxide

$$C_4A_3\bar{S} + 8C\bar{S}H_2 + 6CH + 74H \rightarrow 3C_6A\bar{S}_3H_{32}$$

in the presence of calcium hydroxide

Table 5
Mineralogy of thermally treated aggregates (>500 μm)

Mineral	ISR 1	ISR 2
Quartz	+++	+++
Calcite	++	++
Magnetite	+	+
Hematite	++	++
Rutile		+
Cuprite (Cu_2O)		+

Table 6
Setting time of mortars prepared with thermally treated ISR

Type of mortar	w/c	Initial set (min)	Final set (min)
Standard sand	0.5	330	450
ISR 1	0.6	>1440	>2880
ISR 2	0.6	540	900

In some instances, sulfoaluminate–belite cements have been used to study the formation of oxyanion-substituted ettringites for fixation of heavy metals [5–8]. From a chemical point of view, trivalent ions such as Fe^{3+}, Cr^{3+}, and Mn^{3+} can replace Al^{3+} ions in the crystal structure of ettringite. Ca^{2+} ions can be substituted by bivalent ions such as Mg^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, or Ni^{2+}. Moreover, SO_4^{2-} can be replaced by CO_3^{2-}, NO_3^-, SeO_4^{2-}, or $B(OH)_4^-$ [9–11].

3.2. Verification of the properties of CSA

To verify the fixation of heavy metals by CSA, tests were done using a mixture of 80% calcium sulfoaluminate clinker and 20% phosphogypsum. The composition of calcium sulfoaluminate clinker, assessed by X-ray diffraction and chemical analysis, is as follows: $C_4A_3\bar{S}$: 53.5%, C_2S: 21.2%, C_4AF: 16.3%, perovskite (CT): 9%.

Pastes containing 15 g of heavy metals (Pb or Zn) per kilogram of CSA were prepared. Three pollutants (i.e., heavy metals) were tested: $Pb(NO_3)_2$, $ZnSO_4 \cdot 7H_2O$, and $ZnCl_2$. The composition of three different pastes made is shown in Table 8.

After 28 days of hydration, these different pastes were crushed to get particles smaller than 4 mm. The resulting

Table 7
Water-to-cement ratio of the different mortars

ISR	Treatment	S1	S2	S3
ISR 1	NaOH	0.75	0.52	0.51
	H_2SO_4	0.71	0.52	0.52
	$NaOH + H_2SO_4$	0.70	0.56	0.51
ISR 2	NaOH	0.85	0.64	0.60
	H_2SO_4	0.80	0.68	0.55
	$NaOH + H_2SO_4$	0.80	0.58	0.53
Control	No treatment sand S0	0.50		

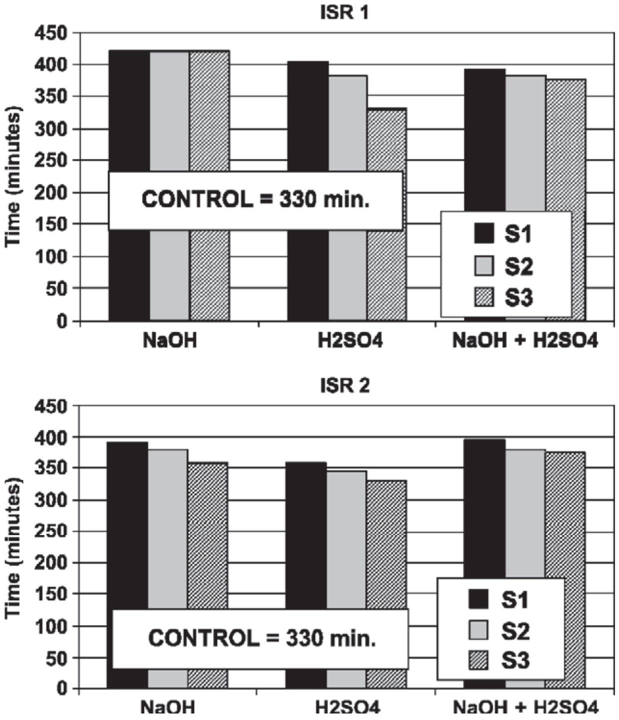

Fig. 1. Initial setting time of mortars containing chemically treated ISR.

sand was leached in deionized water for 24 h at a water-to-solid ratio of 10 (French standard NF X 31-211). Zinc and lead were analyzed in the leachates by inductively coupled plasma–optical emission spectrometry (ICP-OES). Regardless of the sample, Zn and Pb contents were lower than the limit of detection (0.1 ppm), which proved very good fixation and retention by CSA. The high C_2S content of this cement (21.2%) certainly plays a role in the fixation of pollutants: it gives rise to C-S-H gel of zeolitic properties, exhibiting ion-exchanging properties and competing in immobilizing effect.

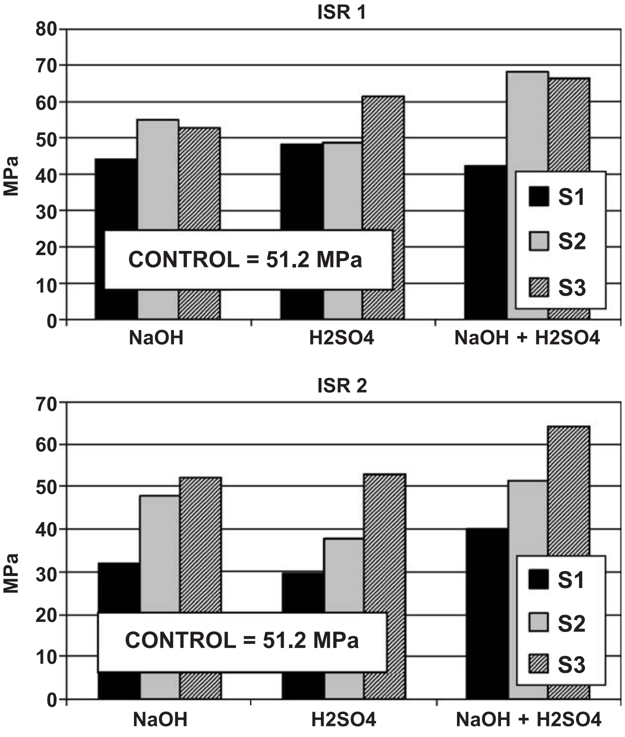

Fig. 2. Twenty-eight-day compressive strength of mortars containing chemically treated ISR.

Table 8
Composition of pastes

Sample	1	2	3
CSA clinker (g)	400	400	400
Phosphogypsum (g)	100	100	100
Water (g)	140	140	140
Pollutant	12 g $Pb(NO_3)_2$	18.5 g $ZnSO_4 \cdot 7H_2O$	15.7 g $ZnCl_2$

3.3. Stabilization of ISR by CSA

A new sample of ISR was used for this study. Its particle size distribution is shown in Fig. 3. All particles were smaller than 4 mm.

The organic content of this sample was 30%. Therefore, ISR was thermally treated at 600 °C to destroy these organics and then analyzed. The chemical composition is shown in Table 9 and the X-ray diffraction is presented in Fig. 4. As pointed out in Table 9, ISR is rich in zinc (3.1%) and lead (1.36%). The main minerals present in ISR are quartz, calcite, magnetite, and hematite.

The valorization of raw ISR was approached with an industrial perspective: the design of a concrete mixture for road construction presenting a minimum 28-day strength of 1 MPa. Such kind of concrete is used for truck tracks in landfills or quarries, or for subbase or base courses for pavements for roadways, highways, and airfields. The composition of this concrete is given in Table 10.

A water-retention agent was introduced in the mixture to prevent desiccation. What is remarkable in this formulation is the ISR/CSA ratio; this value is 3.78, which is very

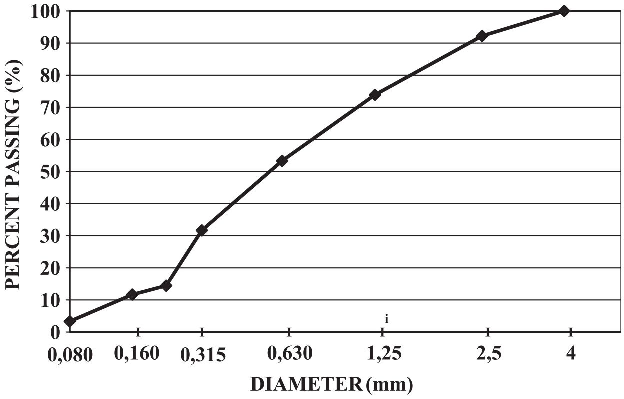

Fig. 3. Particle size distribution of ISR.

Table 9
Chemical composition of ISR after thermal treatment at 600 °C

Main elements	%	Minor elements	ppm
SiO_2	30.70	As	69
Al_2O_3	4.66	Ba	5207
Fe_2O_3	34.35	Cd	56
CaO	10.33	Co	92
MgO	1.84	Cr	1005
MnO	0.26	Cu	6136
Na_2O	1.99	Mo	104
K_2O	0.65	Ni	586
TiO_2	1.38	Pb	13,625
P_2O_5	0.66	Sb	371
LOI	6.53	Sn	606
S_{total}	0.65	Sr	402
Cl	0.31	Zn	31,086

difficult if not impossible to get with normal Portland cement concrete mixtures. The specific gravity of concrete in the fresh state was 1.76 and its 28-day compressive strength reached 4.1 MPa. The specific gravity of normal weight concrete is around 2.4.

At 28 days of age, the concrete was crushed into pieces smaller than 20 mm and placed in a column ($\phi = 80$ mm, $h = 490$ mm) in the presence of deionized water for 3 days. The concrete-to-water ratio was 0.79. The residual water was then analyzed by ICP. Zn and Pb contents were lower than the limit of detection (0.1 ppm), which proved very good fixation and retention by CSA. The oxygen chemical demand was also assessed. Its value was 4217 mg/l, which is high, and proved that CSA by itself is not sufficient to entirely immobilize organics.

Table 10
Composition of concrete (wt.%)

CSA	ISR	Water retention	Water	Superplasticizer
17.15	64.83	0.35	17.15	0.52

4. Conclusions

From this limited investigation, the following conclusions can be drawn:

1. The incombustible fraction of automotive shredder residue, called ISR, can be valorized as an aggregate in concrete either after a thermal treatment at 700 °C followed by a chemical treatment, or directly when using calcium sulfoaluminate cement.
2. Due to its complex chemical composition, ISR may generate dioxins during the heat treatment. A gas treatment must be included in an industrial process and may increase the cost of the recycled ISR into aggregate.
3. Thermally treated ISR cannot be used in concrete because of a drastic delay in setting times of concrete. To avoid such phenomenon, a chemical treatment is necessary, requiring either sodium hydroxide or sulfuric

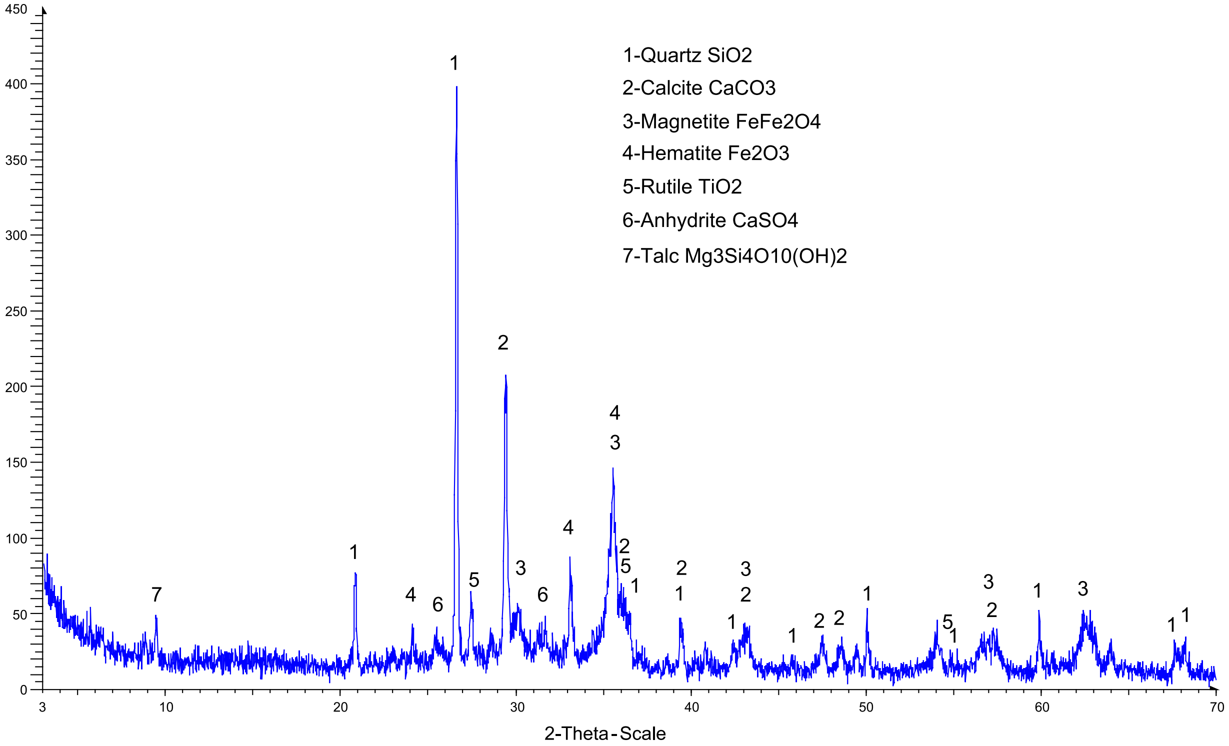

Fig. 4. XRD of ISR after thermal treatment at 600 °C.

acid. In this case, ISR may replace 30% of natural sand in concrete.

4. When mixed with CSA, raw ISR can be used to produce concrete for roadways, highways, and airfields. The quantity of ISR is important in concrete (ISR/CSA = 3.78) and heavy metals (zinc and lead) are efficiently and effectively immobilized, as proved by leaching tests.
5. The use of CSA alone is not sufficient to immobilize residual organics contained in ISR. Further investigation is needed to address this problem.

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