Synthesis of binders using waste materials

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Abstract

Industries produce large quantities of wastes that contain high fractions of silica and lime: sewage sludge, paper sludge, lime sludge, foundry sands, etc. Most of these wastes are currently disposed of in landfills, spread for agricultural purposes or incinerated. Two principal reasons lead to the proposition of environment-friendly alternatives to these present uses: the European directive 1999/CE of 26 April 1999 to limit the harmful effects of landfill disposal of waste, and the progressive decrease of spreading due to regulations.
The project presented here aims to recycle wastes containing large quantities of mineral resources in order to synthesise hydraulic binders at temperatures not exceeding 1000°C. The ultimate goal is to manufacture hydraulic binders from 100% recycled waste, to be used mainly in road-building (backfill, sub-grade, etc.). The energy required for curing is obtained from substitute fuels produced from recycled waste.
The project is divided into 4 phases:

- Construction of a database of waste resources;
- Selection in the laboratory of combinations of wastes for the synthesis of binders;
- Industrial scale tests carried out in a rotary furnace;
- Validation of the results in an industrial application (road test).

This paper reports the results obtained so far.

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1. Introduction

1.1 Project background and objectives

Industrial processes generate large quantities of mineral-rich waste which are often rich in silicon and calcium: water treatment sludge, paper-manufacturing sludge, limed sludge and foundry sands, etc. De-inking sludge produced by papermaking contained 455 000 tons of dry materials in France in 2002, according to Arthur Andersen. The total production of sewage sludge for the United States of America (USA) and countries of the European Union (EU) approaches 17 million tons of dry solids per year (7Mt in USA + 10Mt in EU) [1].

Most of these wastes are at present sent to landfills, spread for agricultural purposes or incinerated [1-4]. Two principal reasons lead to the proposition of environment-friendly alternatives of these uses: the European directive 1999/CE of 26 April 1999 to limit the harmful effects of landfill disposal of waste, and the progressive decrease in spreading due to regulations.

The project presented here is named: Recycling of industrial and institutional waste rich in mineral resources for the manufacture of binders, while saving on natural resources (clay and lime). It aims to recycle wastes containing large amounts of mineral resources, in order to synthesize hydraulic binders at temperatures not exceeding 1000°C. The ultimate goal is to manufacture hydraulic binders from 100% recycled waste, to be used mainly in road-building (backfill, sub-grade, etc.). The energy required for curing is obtained from substitute fuels produced from recycled waste. This project should help to preserve natural resources and is thus in accordance with the European Directive No.91/271 of 21/05/1991 which aims at reducing the volume of waste disposed of in landfills.

The project began in 2006 and this paper reports the results obtained up to now for the production of two kinds of binders: lime- and belite-based binders.

1.2 Project participants

This work is part of a LIFE project, LIFE being the European Union’s financial instrument supporting environmental and nature conservation projects throughout Europe. The industrial organisation leading the project is ARF (north of France). The main activities of ARF are the management, transport and treatment of industrial waste. It is specialised in recycling industrial waste through the preparation of substitute fuels (solid and liquid) designed for use in cement works and lime kilns. The company also focuses on waste recycling and the development of new processing techniques.

LMDC (Laboratoire Matériaux et Durabilité des Constructions), a laboratory of Toulouse University, is the project partner and provides technical help. LMDC is specialised in the development of new materials for civil engineering (innovative materials, eco-materials), weathering and durability of materials, environmental quality and service life of structures (non-destructive testing, maintenance and requalification of structures).

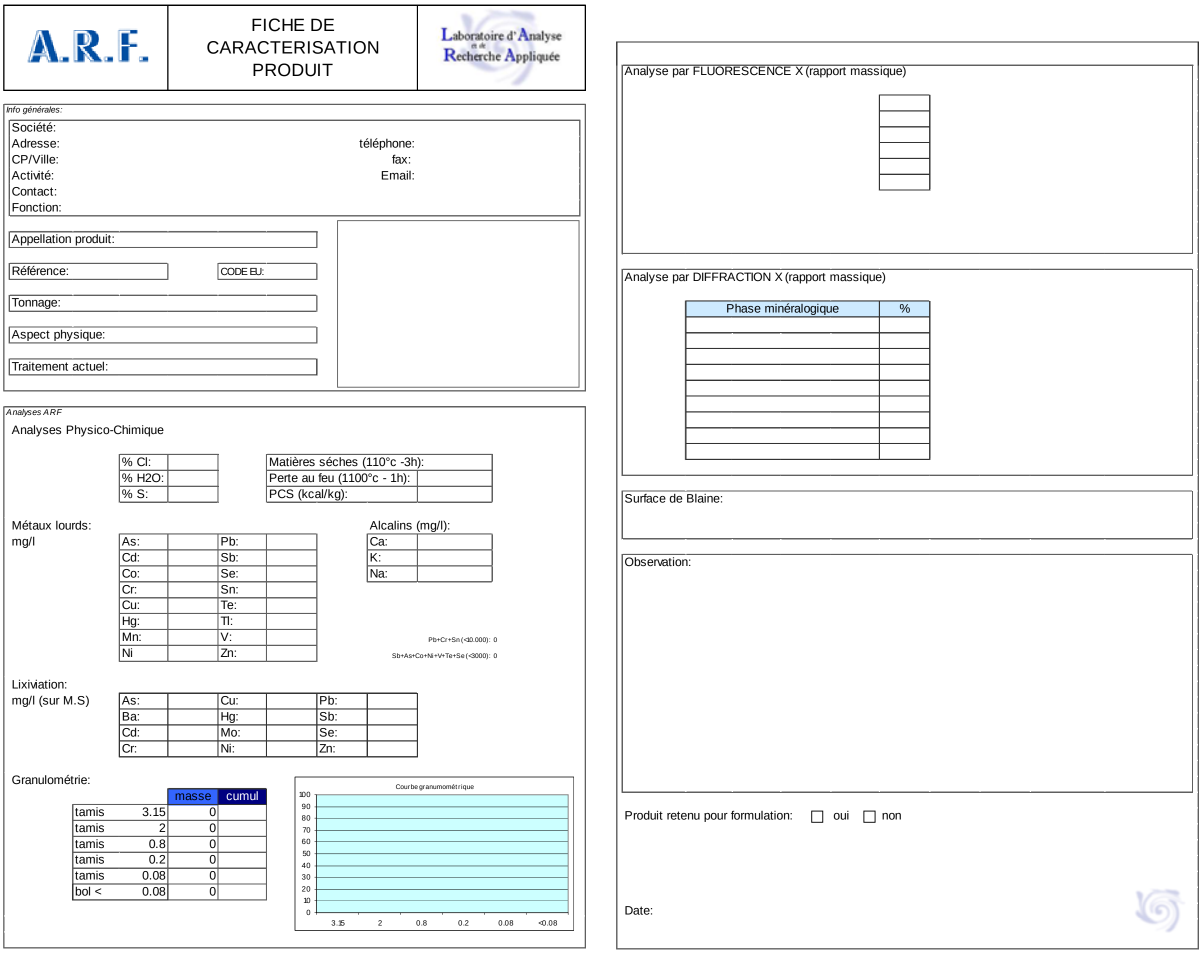
2. Phases of the project and principal results

The project is divided into 4 phases:

- Construction of a database of waste resources;
- Selection in the laboratory of combinations of wastes for the synthesis of binders;
- Industrial scale tests carried out in a rotary furnace;
- Validation of the results in an industrial application (road test).

2.1 Construction of a database of waste resources

This step was initiated in October 2006 and aimed at establishing a list of characterised wastes locally available and liable to enter into the formulation of binders. At the end of the investigation, 44 residues had been identified and characterised. Technical files, like the one given in Figure 1, were filled in for each residue.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FICHE DE CARACTERISATION PRODUIT
Laboratoire d'Analyse et de Recherche Appliquée

Info générales:
Société:
Adresse: téléphone:
CP/Ville: fax:
Activité: Email:
Contact:
Fonction:

Appellation produit:
Référence: CODE EU:
Tonnage:
Aspect physique:
Traitement actuel:

Analyses ARF
Analyses Physico-Chimique
% Cl: | Matières séches (110°c -3h):
% H2O: | Perte au feu (1100°c - 1h):
% S: | PCS (kcal/kg):

Métaux lourds: mg/l
As: Pb: / Cd: Sb: / Co: Se: / Cr: Sn: / Cu: Te: / Hg: Tl: / Mn: V: / Ni Zn:
Alcalins (mg/l): Ca: / K: / Na:
Pb+Cr+Sn (<10.000): 0
Sb+As+Co+Ni+V+Te+Se (<3000): 0

Lixiviation: mg/l (sur M.S)
As: Cu: Pb: / Ba: Hg: Sb: / Cd: Mo: Se: / Cr: Ni: Zn:

Granulométrie:

		masse	cumul
tamis	3.15	0	
tamis	2	0	
tamis	0.8	0	
tamis	0.2	0	
tamis	0.08	0	
bol <	0.08	0	

Courbe granumométrique

Analyse par FLUORESCENCE X (rapport massique)

Analyse par DIFFRACTION X (rapport massique)
Phase minéralogique | %

Surface de Blaine:
Observation:
Produit retenu pour formulation: ☐ oui ☐ non
Date:

Figure 1 – Example of technical file filled in for each of the 44 residues found in the waste database.

The selection of wastes was based on several criteria (Figure 2), the main ones being:

- The amount of residue available
  The long-term expectation is to produce around 27 000 tons of binders each year. Thus, the annual production of waste should be high enough to assure a continuous feed at the plant (> 500 tons/year).

- The chemical composition
  The production of binders requires appropriate quantities of calcium and silicon. Other elements can also be of interest since some impurities (e.g. alkalis) are known to reduce the melting point of materials, thus reducing the burning temperature of the binders.

- The mineralogical form
  Residues containing minerals, in which calcium and silicon were potentially available, were chosen in priority: calcite (Ca), glass (Si), quartz (Si). Minerals very stable at high temperatures (such as refractory minerals) were excluded. It should be noted that quartz-based materials were kept since, although pure quartz has a high melting point, preliminary tests showed that this mineral was very active at 1000°C when mixed with foreign elements.
- The heavy metal contents
  Heavy-metal-rich residues were deliberately rejected since all waste materials were compelled to satisfy the acceptance criteria stated by local authorities. At the entrance of the kiln, the residues must respect the following heavy metal contents:
  - Hg alone < 10 ppm (10 mg/kg);
  - Cd + Hg + Ti < 100 mg/kg;
  - Sb + As + Cr+ Co + Ni+ V + Sn + Te + Se < 1%.

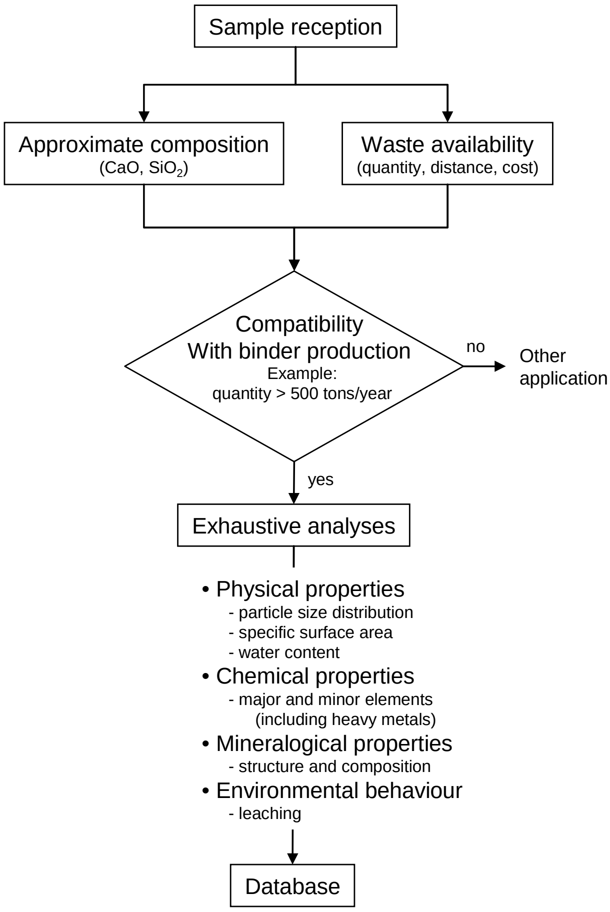

Figure 2 – Method used for the construction of the waste database.

2.2 Selection in the laboratory of combinations of wastes for the synthesis of binders

This task was intended to select specific combinations of wastes in order to burn them in a laboratory muffle oven. Several mixtures of 2 to 5 different residues were prepared, burned at 1000°C and analysed.

Table 1 gives the ranges of lime and belite contents obtained in the laboratory for the two kinds of binders synthesised. For lime-based binders, high free lime contents were obtained, but also significant amounts of periclase and anhydrite. For belite-based binders, scattered results were obtained: between 18 and 75% of β-C_2S (calculated using quantitative X-Ray Diffraction), sometimes with high free lime content. These results depended strongly on several parameters: composition and quantities of residues used in the mixtures, particle size of waste particles at the entrance to the kiln, burning temperature range, type of cooling, etc. Figure 3 shows an example of belite cement having a β-C_2S content around 75%. It was noted that experimental results were compatible with theoretical calculated values. These theoretical values gave the maximum β-C_2S contents that could be obtained from the burned mixtures, calculated from the chemical composition of residues and assuming a stoichiometric combination of 2 moles of CaO and 1 mole of SiO_2. Setting time measurements made on these binders gave values between 2 and 8h.

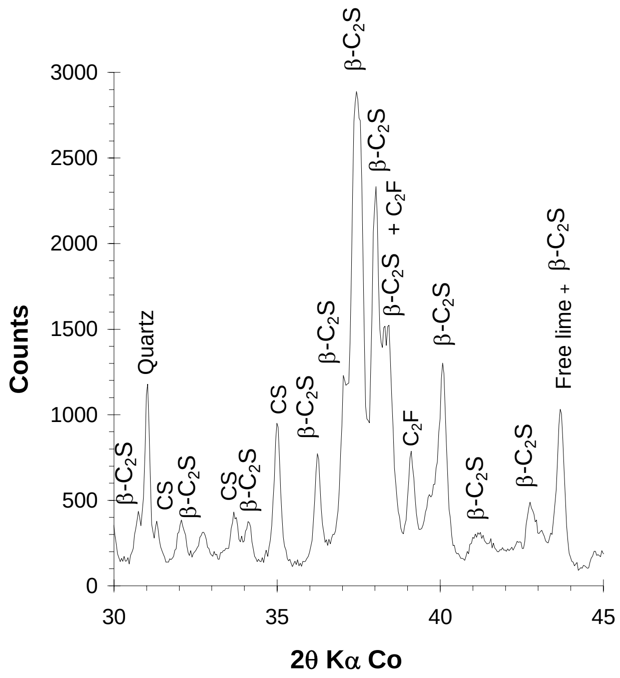

Figure 3 - X-ray diagram of a belite binder synthesised in the laboratory

In addition to β-C_2S and free lime, the synthesised cements contained other minerals (Table 1), mainly periclase, anhydrite, wollastonite and gehlenite. The presence of wollastonite ($CaSiO_3$), which is a very stable mineral, showed an incomplete combination of calcium, although free lime was still present in the mixture.

This problem could be related to slow diffusion processes, due to the use of a static oven. It was thought at the time that this problem would probably be fixed by the use of the rotary kiln. Gehlenite ($Ca_2Al_2SiO_7$) is a poorly reactive mineral and can be considered as inert compared to β-C_2S. To avoid the synthesis of this compound, it would be necessary to use raw materials without available aluminium.

Alinite-based clinker was also tested in this study. This binder, which includes large quantities of chlorine (3-10%), has a similar hydration process to alite. It can be produced at lower temperature and it is known to be more reactive than belite [5]. Due to industrial and legislation restraints (presence of chlorine), this binder has only been tested at a laboratory scale.

Table 1 – Minerals present in synthesised binders at laboratory and industrial scales

		Lime-based binders		Belite-based binders	
		Laboratory	Industrial	Laboratory	Industrial
Range of free lime content (CaO)		75-80%	50-60%	2-28%	13-36%
Range of belite content (β-C_2S)		0-5%	12-16%	18-75%	13-16%
Impurities – reactive*					
Periclase	MgO	++++	+++	++	+
Anhydrite	$CaSO_4$	++	+	++	++
Portlandite	$Ca(OH)_2$	+	++	+	+
Impurities – inert**					
Quartz	SiO_2	+	+	+	++++
Calcite	$CaCO_3$	0	+++	0	+++
Wollastonite	$CaSiO_3$	0	0	+++	+++
Perovskite	$CaTiO_3$	+	++++	0	++++
Gehlenite	$Ca_2Al_2SiO_7$	+	++	++-++++	++++
Hematite	Fe_2O_3	0	++	0	0

++++: > 10%; 5% < +++ < 10%; 2% < ++ < 5%; +: < 2%
* considered as active in basic environment; ** considered as inert in basic environment

2.3 Industrial scale tests carried out in a rotary kiln

Some of the combinations found in the previous phase were tested on an industrial scale. So far, two and four tests have been carried out to produce lime-based and belite-based binders, respectively. These tests were done in a 60m-long, 3.2m-diameter rotary kiln (Figure 4) at a temperature of around 1000°C. A fraction of the fuel was replaced by a highly calorific residue. For each test, approximately 50 tons of mineral residues were used. The burned materials were air cooled at the exit of the kiln.

The binders were then analysed to determine some of their characteristics, including their chemical and mineralogical compositions. Table 1 gives the ranges of free lime and belite contents obtained for the two kinds of binders synthesised.

Comparing the laboratory and industrial scale tests, it is obvious that the industrial tests were less efficient in producing lime and β-C_2S phases, especially for belite-based binders. The small quantities of active phases were related to the large amounts of unreacted minerals such as quartz and calcite, and impurities produced in the kiln (perovskite, wollastonite, gehlenite).

Several reasons could probably explain these results, the main ones being:

- The large diameter of some calcareous products at the entrance of the kiln led to the formation of free lime aggregates which were not broken down during the burning process. Consequently, a lime deficit in the kiln led to the production of wollastonite (CS) instead of β-C_2S.
- A part of the lime was consumed by the titanium present in the highly calorific residue, to form perovskite (calcium titanate), which is very stable at room temperature and in a basic environment.
- A temperature below 1000°C in the kiln could explain the large quantities of unreacted minerals still present in the binders. The difficulty of keeping a high temperature could be due to the presence of the highly calorific residue, which did not have the efficiency of conventional fuel.

Other tests will be carried out to adjust the industrial conditions.

Figure 4 – Rotary kiln used for industrial scale tests

2.4 Validation of the results in an industrial application (road test)

In order to qualify the synthesised binders in a road-work test, an experimental road structure was built on the production site of the binders (Figure 5). This structure of $48m^2$ and 0.6m depth was built in November 2008 and will be studied for 12 months (Figure 6). Mechanical tests will be performed and percolate water, which is isolated in tanks, will be periodically analysed.

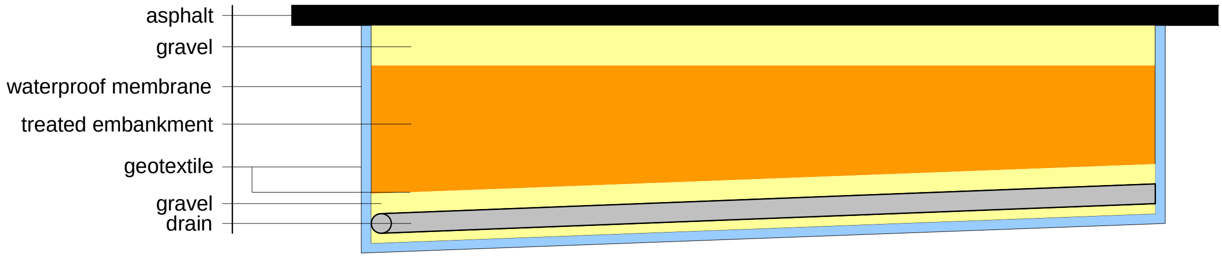

Figure 5 – Profile of road structure for the test of lime-based binder used in treated embankment.

Figure 6 – Construction of the road structure for the test of lime-based binder (used in treated embankment).

3. Conclusion

The aim of the project is to produce binders from mineral-rich waste using a special preparation process based on residues. The process intends to save the noble mineral resources conventionally used in the production of binders. Main applications concern the production for road-making. The project comprises 4 phases:

- Construction of a database of waste resources: 44 residues were identified and characterised.
- Selection in the laboratory of combinations of wastes for the synthesis of binders: for lime-based binders. High lime contents were obtained, but also significant amounts of periclase and anhydrite. For belite-based binders, between 18 and 75% of β-C_2S was obtained, sometimes with high free lime content.
- Industrial scale tests carried out in a rotary furnace: up to now, these tests have been less efficient in producing lime and β-C_2S phases, especially for belite-based binders. However, the main problems have been identified (particle size of waste materials, low burning temperature, parasite reactions in the kiln)
- Validation of the results in an industrial application (road test): the monitoring of an experimental road structure will continue in the coming year.

Acknowledgment

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References

[1] EUROSTAT, http://epp.eurostat.cec.eu.int.

[2] EPA, Biosolids Generation, Use, and Disposal in the United States, U.S. Environmental Protection Agency, Municipal and Industrial Solid Waste Division, Office of Solid Waste, EPA530-R-99-009, September 1999.

[3] CH2M Hill Canada, Biosolids Generation, Treatment, Use and Disposal in Canada, Opportunities for Energy Recovery and Greenhouse Gas Reduction Report, prepared for Environment Canada, 2000.

[4] Apedaile E., A perspective on biosolids management, Canadian Journal of Infectious Diseases and Medical Microbiology, 12 (4) (2001) 12-25.

[5] Odler I., Special Inorganic Cements, E&FN SPON, London and New York, 2000, 395p.