



LIFE ENVIRONNEMENT PROPOSAL n°LIFE06 ENV/F/000124 ARFVALORMAT

Project acronym : ARFVALORMAT

APPLICANT : Société A. R. F.

Recycling of industrial and institutional waste rich in mineral resources for the manufacture of binders, while saving on natural resources (clay and lime)

LAYMAN'S REPORT
[01/10/2006 - 30/06/2009]

A.R.F.

**ARF
valormat**



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1 – Project context and objectives

1.1 – Environmental context

Industry generates high quantities of waste that is rich in silicium, lime and carbonate, such as water treatment sludge, paper-manufacture sludge, limed sludge or foundry sands.

The main forms of disposal or treatment of this type of waste are presently landfilling, land spreading and incineration.



With the European Directive No.1999 of 26/04/1999 aimed at reducing the negative effects of putting waste into landfill and with the phasing out of land spreading owing to increasingly severe regulations, it has become essential to find alternatives that are fully in keeping with present environmental concerns.

1.2 – Objectives and Project description

It is in response to this need that ARF is proposing an innovative process for manufacturing hydraulic binders and/or inert materials the essence of which is to substitute all or part of the quarried clay and lime with minerals prepared from waste.

The project includes the construction of a **database of sources of waste** from which combinations of substitute minerals will be selected. After a phase of laboratory tests, these mixes will be subjected to industrial scale curing tests further to which the hydraulic binder manufacturing process can be established. Finally, the end products (hydraulic binders, inert materials) will be qualified according to their applications (road sub-layer, backfill, etc.).

1.3 – Players in the project:

 Beneficiary	<p>ARF Activités de Recyclage et de Formulation [59330 SAINT REMY DU NORD / 02800 VENDEUIL]: ARF is specialized in the recycling of industrial waste in the form of fuel or substitute minerals used mainly in cement works.</p>
 Partner	<p>Laboratoire Matériaux et Durabilité des Constructions – LMDC (Materials and Durable Construction Laboratory) is a university research laboratory working in the field of civil engineering materials science, located at the Ranguel campus in Toulouse.</p>

2 – Methods and results

The process development will be in three main phases:

- Construction of a database of waste sources – selection in the laboratory of combinations of substitute minerals to be subjected to cure tests;
- Cure tests on an industrial scale (rotary furnace); analysis of end products; shortlisting the efficient combinations with a view to validating the process.
- Validation of the process for manufacturing inert materials and hydraulic binders, innocuity test, mechanical test and qualification of the end products according to their applications (road building, backfill).

2.1 – Database construction

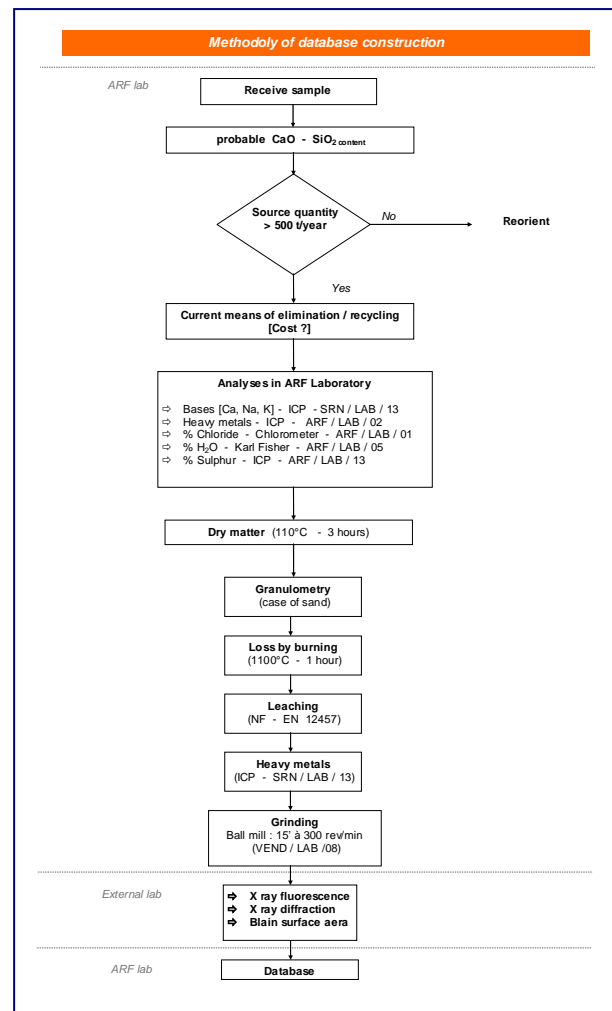
☑ Methodology

Work to identify possible sources of work was conducted by ARF between 2003 and 2005. At that time, ARF set down a methodology for drawing up a database of waste, completed by a procedure for testing combinations of sources in the laboratory.

After completely reviewing the source selection procedure and on the basis of the new structure of the database established at the start of the LIFE programme in October 2006, the database of waste sources was completely updated and enriched.

Each source was studied according to the set selection procedure, including in particular:

- Analyses by the ARF Laboratory:
 - Physical-chemical analyses: % Cl (chlorine), % H₂O (water), % S (sulphur), % Dry materials, % loss by burning, calorific power;
 - Heavy metal content;
 - Leaching;
 - Granulometry;
- Analyses performed in an external laboratory:
 - X ray fluorescence to define the mineralogical composition of the product;
 - X ray diffraction to determine the form in which the mineralogical elements are present in order to verify their reactivity;
 - Blaine's area giving the specific area of the product and its reactivity potential.



Each source was entered into the database in the form of a product specification sheet [photo of the waste, contact details of the producer of the waste and its business sector, product name, sample reference, annual tonnage, physical appearance of the product, present treatment of the waste and cost, results of physical-chemical analyses, results of X ray fluorescence and X ray diffraction analyses].

Results

On 30/06/2009 (End of the project), the database contained **50 fully identified** sources, 13 of which are graded as interesting [151 500 tonnes] and 9 as potentially interesting [155 644 tonnes].



A013 : Boue de papeterie

Technical developments are constantly monitored so as to enrich the database, thus ensuring the perennality of the programme.



A041 : Sable de fonderie

2.2 – Mix formulation & laboratory tests

Methodology

Based on the sources listed in the database, ARF, in cooperation with LMDC, determined mix formulations according to the stoichiometry of the chemical reaction of the C₂S and CaO. For this, it used the laboratory phase source mixing test procedure.

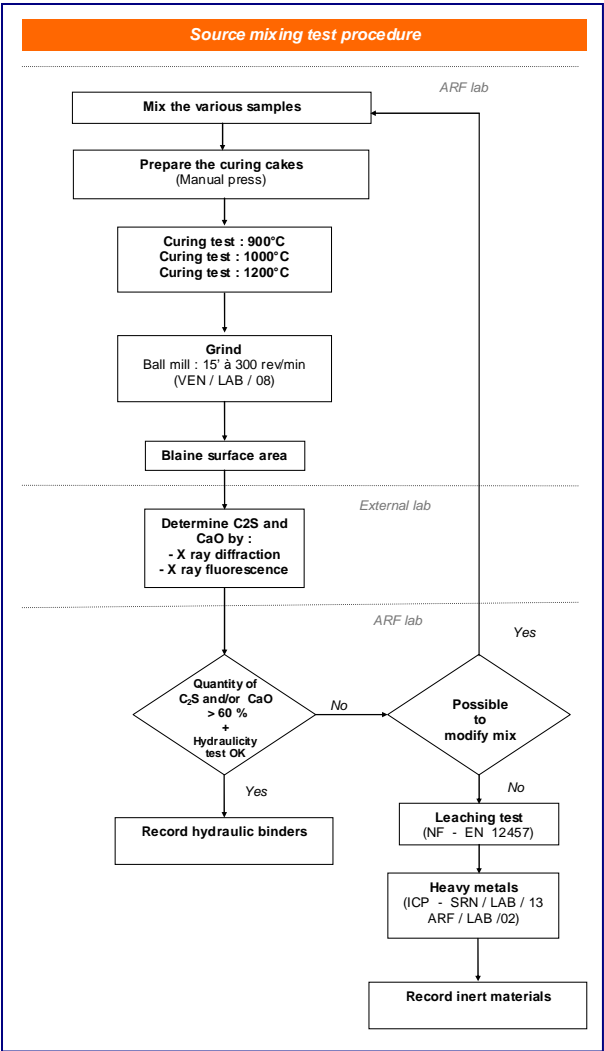
Each component is weighed in a bowl. Water is then added to form a sludge of even consistency. The “raw material” is thus obtained (the quantity of water added is recorded in the test log). After various tests on different types of crucible (alumina, stainless steel, refractory brick), we decided to use the refractory bricks (same composition as the furnace bricks). The raw material is placed on the bricks and introduced into a static muffle furnace at around 500°C. The temperature of the furnace is increased to 1100°C in around 20 minutes and curing lasts around one hour.



Weighing the components



Mixing [with added water]





Preparation of the cure test cakes



Test cakes after curing for 1h at 1100°C



Product after crushing and sieving

Results

21 mixes has been tested, 6 of which were refined via additional tests on derived formulations. 5 mixes has been selected for curing tests on an industrial scale.

Example of formulation: EA.008.02

- A001 : Industrial sludge
- A032 : Food-processing waste
- A039 : Solid fuel boiler ash
- A042 : Clay sludge
- A047 : Silica fumes
- Lime

A001	A032	A039	A042	A047	POUSSIER
20.0%	20.0%	10.0%	39.0%	1.0%	10.0%



2.3 – Industrial scale curing tests

Methodology

Two types of mix preparation for feeding into the rotary furnace were used during these tests.



Semi-wet method:

- Preparation of mixes in sludge form in a mixer [with added water to ensure a homogeneous mix]
- Introduction into furnace via a sludge pump



Dry method:

- Mix preparation using a mechanical shovel at the Saint Rémy du Nord site and transfer to Vendeuil
- Introduction on conveyor belt and infeed hopper of the rotary furnace




Formulations tested

Test no. 1 [semi-wet method]: E.A009-3

- A001: (Industrial) treatment works sludge
- A018: Boiler ash
- A019: Filtered ash
- A032: Food-processing waste
- A042: Clay sludge
- Lime addition


A001	A018	A019	A032	A042	Calcaire
9.0%	4.0%	9.0%	18.0%	36.0%	24.0%



Test no. 2 [semi-wet method]: E.A013

- A001 : (Industrial) treatment works sludge
- A032 : Food-processing waste
- A042 : Clay sludge
- A049 : Refractory waste


A001	A032	A042	A049
37.0%	37.0%	18.0%	8.0%



Test no. 3 [semi-wet method]: E.A010

- A001: (Industrial) treatment works sludge
- A032: Food-processing waste
- A013: Paper mill sludge

A001	A013	A032
33.3%	33.3%	33.3%





E.A010 après cuisson & broyage

Test no. 4 [semi-wet method]: E.A003

- A001: (Industrial) treatment works sludge
- A016: Lime dust
- A032: Food-processing waste
- A031: Wet ash

A001	A016	A031	A032
33.0%	33.0%	17.0%	17.0%





E.A003 brut après cuisson

Test no. 5 & 6 [Dry method]: E.A021

- A001: (Industrial) treatment works sludge
- A032: Food-processing waste
- A049 : Refractory waste
- Lime addition

A001	A032	A049	calcaire
22.0%	22.0%	11.0%	45.0%



Results

ARF realized:

- 4 tests prior to introducing the material [dry method]
- 4 industrial scale curing tests [semi-wet method]
- 2 curing tests for process validation [dry method].

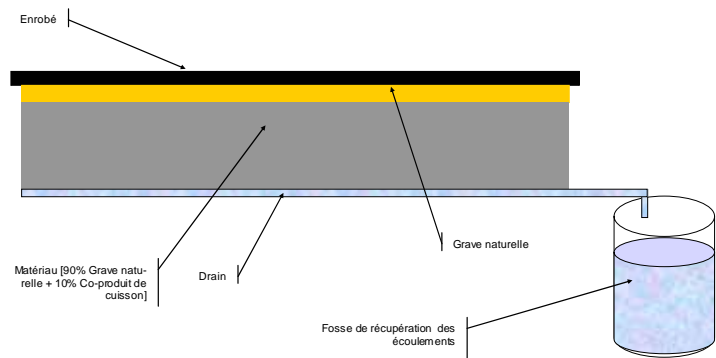
The co-product of test no. 6 have sufficient hydraulic properties to be used in road sub-layer. This test was using the same mineral preparation of the test no. 5 but with extra energy and at the lower infeed rate of 2T/hr.

2.4 – Product classification and experimental plot

☑ Méthodology

With regard to task no. 3 which was started on 01/11/2007, the Third-party Expert drew our attention to the fact that the analyses initially planned for classifying the curing co-products would not be sufficient. Supplemental to the analyses for determining the hydraulic properties of the co-products (setting and stabilization times, pouzzolanicity, tensile strength) and simple leaching tests (environmental safety), **an extra phase** needs to be added for observing the long term behaviour of the co-product when used in road-building materials.

A full scale experiment was thus conducted on the basis of the ADEME agreement for "Lysimeters and experimental plots". An implementation and monitoring scenario (physical-chemical and geotechnical type of analysis, frequency, etc.) specific to our project was developed by Pierre Silvestre.



The plot tested has to faithfully reproduce the type of use proposed (thickness, construction, other fills used, etc.) in order to obtain as representative a result as possible.

The recommended time for monitoring this test should correspond to a hydrological year covering the 4 seasons.

☑ Characteristics of the experimental plot

The experiment was conducted at the ARF site in Saint Rémy du Nord, and the monitoring operations and controls were put in place from 04/11/2008:

- **Curing co-product tested:** E.A021 [55 % waste – test no. 6]
- **Quantity used:** 6 to 8 tonnes (10% of the structure of the substrate material)
- **Plot size:** 48 m² and 0.60 m deep
- **Experiment duration:** 12 months [14/11/2009]



An adjacent plot 8 m² without tarmac completes the system. The percolation water is isolated in the same way in another tank for monitoring and control.

Monitoring & Control provisions:

The experiment should enable us to appraise the geotechnical and environmental feasibility of the project. The observations, measurements and controls therefore concern these two aspects:

- Geotechnical monitoring of the material after mixing: granulometry, etc.
- Environmental control of the material after mixing: leaching, upwards percolation, etc.
- Measurements and analyses on water recovered from the plot (Ph, TOC, metals, major components, salts, PCDD/PCDF, etc.: 8 to 10 measurement series
- External control of the complete plot experiment
- Summary of results with the source term expressed in terms of flow rate



The results will then be compared to a natural flux reference standard.

Interim results

In April 2009 we obtained 4 series of measurements.

These initial results indicate that:

- the water ingress is under control for the tarmacked plot (less than 10% effective rainfall);
- for all the chemical parameters, we are still in the physical-chemical balancing phase. All the values obtained are in keeping with the provisional target values set by the Meeddat. (provisional guide v12 –May 2009). The two parameters that come the closest to these targets are total chromium and molybdenum;
- the fluids leached correspond to a unit flux of the same amount as the natural flux encountered in metropolitan France.

A final report will be written by Pierre Silvestre, our third party expert. The full results will be given in terms of the leaching of chemicals into the environment [flux per m² per year of occupation of the ground], concentrations at the output of the test structure, the ratio of leached substances to the weight of material tested [mg/kg], time and L/S [liquid/solid]. The aim of this experiment is to provide us with data which will enable this type of curing co-product to no longer have the status of waste.

3 – Environmental impact / environmental benefits

The ARFVALORMAT project has enabled us to develop a process for manufacturing hydraulic binders that could be used in road building, based on 55% waste. The studies regarding the impact of this product on the environment are not yet complete but the initial results from the experimental plot have proved positive and we should, by the end of the experiment, have significant information for the status of the waste used for this production to finally be changed.

The outcome of this project will be to offer a new use in the form of a finished, commercializable product to waste that would formerly have been disposed of in landfills, agricultural spreading (slurry), used to fuel cement works or incinerated in a special plant.

This innovative project also has an unquestionable advantage for the environment:

- By preserving our natural resources (use of waste instead of pure clay);
- By proposing an alternative to and thus reducing landfill disposal (restricted to the end waste products only);
- By offering an environment-friendly solution to the treatment of special industrial waste in that it allows products or materials that would formerly have been disposed of to be reused.

We can therefore assert that the ARFVALORMAT programme, supported by the European Union, will ultimately prove of great benefit to the environment, by contributing to improving the management of the waste produced in the EU and by complying with the guidelines of Directive 2008/98/CE of the European Parliament and Council of 19/11/2008 on waste, one of the objectives of which is to strive towards a European society that favours recycling.

4 – Transfer of project results

The manufacturing process developed by ARF to produce hydraulic binders is highly reproducible both at a domestic and European level. It can be easily duplicated using industrial plant similar to that used in Vendeuil: rotary furnace of the type used in cement works or lime kilns, modest in size with a production capacity of under 20 tonnes per hour. It is based on the knowledge acquired during and at the end of the demonstration programme in the form of a database of waste sources, an agreement and flow chart of the production process.

In France, the problem remains however that curing co-products [hydraulic binders] continue to have the status of waste and no procedure has yet been put in place to declassify the product as a "secondary raw material".



Other European Union countries appear to be more advanced in this field. By integrating European Parliament and Council Directive 2008/98/CE adopted on 19/11/2008 into French law, this state of affairs should soon change.

5 – Future prospects

On the basis of the results obtained during the ARFVALORMAT programme, it would appear necessary to conduct further, more in-depth research, working with the Toulouse LMDC INSA, essentially in order to:

- **improve the rate of substitution** of natural mineral resources by waste (55% waste in the formulation tested in the experimental plot): pursue our technology watch on the database and test new formulations (lab and full scale tests);
- **validate the safety of the products obtained** with regard to the environment and ascertain their status as a secondary raw material ;
- **diversify the application categories** for our curing co-products.

4 – Contacts

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