SYNCRETE
A HIGH EFFICIENT POLYMER CEMENT EMBEDDING MATRIX FOR WASTE PROCESSING

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ABSTRACT

A polymer-cement concrete, SYNCRETE, has been developed under an agreement between SYNCRETE SA, owner of the patent, and STMI, subsidiary of the French Electricity Board, EDF, and the French Atomic Energy Commission, CEA, for nuclear cleansing services, to be used in both waste processing and waste transportation fields.

Combining the advantages of usual concrete (safety, easy operations, cheapness) and polymers (leachability, quick hardening, and good encapsulation), this product seems to be the most cost effective matrix for either usual or specific alpha and beta-gamma low and medium activity waste encapsulation. Its exceptional mechanical properties allow SYNCRETE in the same way to be a well suited basic material for transportation and storage container manufacturing.

In the first step, a water and polymer emulsion is prepared and then mixed with the dry charge including cement and catalyst. The nuclear waste can be added in the first or the second step, depending on its origin. The interpenetration of polymer chains and hydrated silicates give to SYNCRETE an exceptional stability and physical properties in a very short time: 70% of the mechanical strength is reached after less than 3 hours.

The first tests have been performed on physical properties (compressive strength over 1000 bars, i.e. 100 MPa, cracking tests, water absorption, chemical resistance, fire tests, UV and freezing behavior, irradiation behavior, decontamination operations, and specific ions release in water). All these tests have given results that incite us to start a complete characterization test program with active wastes.

SYNCRETE properties, as well as those of the basic products, give all the operations enhanced safety, either in handling or processing; as for instance, polymer is shipped from the factory in a 5% preemulsion form.

The mechanical properties enable us to consider that SYNCRETE could be a unique material for substituting for reinforced concrete or any other material in transportation or in storage casks and containers.

THE PRODUCT=SYNCRETE

SYNCRETE (Synthetic Concrete) is a composite matrix which associates an ordinary hydraulic cement and a thermosetting polymer mixture.

General Remarks on Polymer Concrete

This name usually covers 3 product categories which for a few years have been the subject of several studies in the world:

- the polymer impregnated concretes are the standard type concrete where the cement porosities are as much as possible filled with a polymerizable mixture through an autoclave,
- the polymer concretes contain only agregates and a polymerized mixture with the exclusion of any hydraulic binding,
- the cement and polymer concrete almost simultaneously involve a cement hydration reaction and the polymerization of the organic compounds. SYNCRETE does belong entirely to this latter family but under RRCC classification, it is a polymer which reacts to cement. SYNCRETE is thus ruled by three successive reactions which finally combine with each other, they are:

- an emulsion water hydration reaction with part of the cement,
- a polymer/cement reaction through the cement double silicates C^2S,
- a polymer reaction with its hardener since it is freed from its emulsion water.

SYNCRETE Composition

SYNCRETE product has been given the patent Nr 76 24 928 and three associated application patents, Nr 77 33 824, the two others on their way to being registered in most of the industrialized countries.

SYNCRETE is a varied proportion mixture of polymers which belong to the families mentioned in the basic patent, cement inert additives (sands, agregates), possible organics or minerals, water and a catalyzer.

A first phase polymer-water emulsion is prepared, then mixed to the whole cement, inert filler and polymerization catalyzer. This catalyzer also enables water from the emulsion which is immediately caught by the dement hydration reaction. The close imbrication of reticulated polymer chains and the non-hydrated cement grant the final product a very important stability and excellent mechanical properties.

SYNCRETE sets in a very short time; in less than 3 hours, the product achieves 70% of its physical properties; it sets within 30 minutes.

Its physical properties depend on the water/cement ratio and consequently on the water/polymer ratio within the emulsion. The variation of this last ratio enables the passage, when water content is low from a polymer concrete into a cement and polymer concrete for an emulsion water percentage ranging between approximately 10 to 60%. Above 60%, the properties are similar to these of a quick hardening conventional cement.

Practical Application Principles

SYNCRETE is made in a two phase preparation which can follow each other or in a two phase preparation separated in time from each other:

- Preparation of a polymer aquaous emulsion with a water content previously defined. Function of the goals to be achieved (Mechanical characteristics, incorporation rate, setting time, encapsulated products compatibility...). This emulsion is carried out with a high rotation speed emulsificater, which allows a large screening of water droplets inside the polymer phase: smaller than 12 microns.
- Mixing the smaller obtained emulsion with the dry-fillers (cement catalyzer, possible additives) thus requiring a standard type device (concrete mixer, mixing mill) so as to obtain a ready to set homogeneous mixture.

It is possible to stabilize the emulsion so as to mix it with cement several weeks after it has been prepared. In this case it can be achieved by mixing it with a polymer mixture which has thixotropic properties so that transportation is made easier.

It is also possible to prepare an emulsion with a very fluid polymer so that this cement emulsion mixture can be compared with a fluid cement grouting.

It is noted finally that SYNCRETE applications could also cover the soluble polymerization practical application which would possibly allow the suppression of the emulsion phase.

Physical Properties

SYNCRETE practical application soon leads to a product, the mechanical characteristics of which go largely beyond those of standard concretes. As mentioned above, this is the consequence of the interpenetration of the silicates crystalline network which formed during cement hydration of the molecular network issued from the polymerization.

These reactions are very fast. After three hours, the final mechanical properties represent about 70% of the final properties, and after 24 hours more than 90%.

Several tests concerning the physical properties have been conducted on SYNCRETE test bars containing basic polymer with a water/polymer ratio ranging from 10 to 40% and a variable agregates content in the cement.

From these tests, we can state the following characteristics:

- Compression Resistance: 80/85 MPa average. Values which can be obtained from a good traditional concrete.
- Traction Resistance: (Bresilian Test) The difference is even more obvious: 12 to 15 MPa for SYNCRETE (1 to 2 MPa for a good ordinary concrete).
- Flexion Resistance: 18 to 20 MPa.
- Cracking behavior: SYNCRETE resistance to crack development is a lot better than that of an ordinary concrete or of a pure polymer, since there are three simultaneous reactions to ensure its cohesion.
- Fire test: the reaction to fire has been tested on a 15mm SYNCRETE plate according to the english standards. In this respect, SYNCRETE shows much better qualities than a hard polymer, and slightly inferior ones to those of a standard concrete.
- Water Absorption: SYNCRETE total immersion tests have shown:
  - after 70 hours 0.10% ponderal increase
  - after 10 days 0.25% ponderal increase

These values are very low compared to those of a standard concrete. They are due to the SYNCRETE very low porosity and consequently, to its very low permeability.

- Chemical Resistance: SYNCRETE can be easily maintained through a high salts content water, like sea water or very saline effluents. It adapts also with agregates from sea origin or with salty non-washed agregates.

A very high resistance of SYNCRETE to the main agressive chemical agents can be noted, and peculiarly, a very high resistance to 10 to 20% acid solutions during a twelve months period.

Its behavior is also very good when faced with mineral oils and petroleum (test duration: 5 months).

It is good in presence of alcaline solutions even concentrated.

- Ultra-violet Resistance: After a twenty month exterior exposure (Western Australia) and UV lamps exposure, no trace of damage has been noticed on the surface.
- Frost Resistance: After more than 12.000 frost/defrost cycles 3 years tests carried out at the laboratory, the average weight loss on three samples was 0.32%.
- Thermal characteristics: Thermal expansion coefficient (between 25°C and 100°C):

  - $3.10^{-5} \pm 0.25\ 10^{-5}$ cms/cm/)C

  Thermal conductivity: 0.9 ± 0.05 Watt/m/°C

Also to be noted is the very low exothesmic effects with SYNCRETE setting.

- Abrasion Resistance: For a 1.000 cycles, a 3.2 gr. weight loss was measured on SYNCRETE with a TABER wheel, while on an ordinary concrete, the loss in the use of a special fillers enables us to improve this resistance.
- Radiation Resistance: SYNCRETE, exposed to a 10^9 rad integrated total dose during a few hours or placed in a 10 rad.h-1 field during

a six month period, did not show visible damage.

- Decontamination: A SYNCRETE plate, contaminated by beta-gamma emitter, has been decontaminated by 99.82% through washing with diluted nitric acid and detergents.

Application to the Conditioning of Radioactive Waste Products

Because of the good properties mentioned above, SYNCRETE is naturally predisposed to numerous uses as regards to the conditioning of low or medium activity waste of radioactive source.

For example in a non-exhaustive way:

- The "process" radwaste products from the nuclear power plants (spent ion exchanges resins, evaporation concentrates, various sludges, filter cartridges, decontamination effluents) owing to its good mechanical and permeability characteristics which let us assume a good lixiviation resitance and also to its good resitance to chemical pollutants.

- The graphite sludges from the gas-graphite plants.

- The organic and mineral oils and decontaminated solvents.

- Some technological waste products.

- The whole of radwastes because of the very good confinement which has been achieved.

It will be possible to carry out this application either on fixed or centralized equipment per site or by using mobile units.

In all cases, these units will be composed of:

- a 5% water pre-emulsified polymer storage,

- a cement storage,

- a catalyzer storage,

- An emulsification device,

- a mixing device.

The emulsificater will be fed with the polymer preemulsion and titer with the waste to be encapsulated, if it is liquid, or if it can be hydraulically transported, or with water, if it is solid waste.

The cement, the catalyzer and the radwaste, if solid, are first fed into the encapsulation container.

This container is then positioned in the mixing unit where the emulsion is introduced. The mixing can be made either with a consumable blade system drawn by a shaft, or by blades fixed on the side of the container which itself is being moved with an adequate movement.

SYNCRETE will then be directly generated in its storage volume.

SYNCRETE practical applications can be carried out with simple equipment, which does not require the development of new equipment.

No optimization of an encapsulating procedure has been carried out as yet on one of the radwastes mentioned above. However, some feasibility tests have been carried out in a laboratory on some of these radwastes. The first observations regarding the volumic incorporating ratios which could be reasonably expected, without prior processing, in the final block, can be pointed out as follows:

- for spent ions exchange resins: 60%

- for liquid sludges and concentrates: 30 to 35%

These rates could be adjusted and most probably increased after a specific study. However, it is to be noted that a technological limit exists as regards to the incorporating into the final matrix of a higher to 50% water volume, since the water/cement ratio then becomes too high.

Safety of the Process

SYNCRETE properties as well as the delivery state of the involved products have in its favor as regards to the most important criteria: the safety.

The only possibly toxic or dangerous products which come into the polymer composition are delivered in the form of a 5% stable water pre-emulsion, which does not present anymore potential risks than a pure organic product.

Besides, SYNCRETE's practical application as it has been described above, can be carried out while taking into account all the safety requirements related to operating conditions and of the products involved.

Finally, the characteristics of the final produced block of SYNCRETE let us assume that the safety constraints on a waste disposal site are perfectly complied with.

PROCESS CHARACTERISTICS

As regards the application of an encapsulating matrix to the conditioning of radioactive waste, it is important to know the behavior of the matrix,i.e., waste product association for each type of considered waste.

This characterization must comply with ANDRA specifications and to CEA/BECC requirements, as the responsibilities of the waste producer.

At present, no trial program has been realized on SYNCRETE characterization for an application to radioactive waste.

However, from incorporation tests achieved in a laboratory, it has been possible to set up with an acceptable accuracy the required parameters in the pre-characterization phase under laboratory cold conditions.

Test Results

The following results have been obtained using $4 \times 4 \times 16\ cm^3$ or cylindric ($h = 5$ cm, $\emptyset = 4.5$ cm) test probes, containing approximately 50% boron saturated ion exchange resins, after immersion into a saturated boric acid solution during several days (% in volume).

The resins are the same type resins as those involved in APG circuits of the PWR power plants (mixed bed=sulfonic polystyrene or quaternary ammonium).

A) Physical and mechanical properties:

Density	1.600 Kg/m^3
Hardness	not measured
Compression resistance	50 MPa
Water porosity and permeability	very low

B) Control of the encapsulated product homogeneity:

Test probes cuttings (4 x 4 x 16) realized during flexion tests have enabled to check the good qualitative homogeneity of the encapsulated product. The resin bids repartition is perfectly uniform after in laboratory mixing. However, it must be confirmed on a scale 1, according to the chosen mixing system.

C) Matrix-waste compatibility:

SYNCRETE chemical tolerance and stability have been indicated. The test probes section examination allows a check that no phenomenum occurs with time.

As regards the reciprocal matrix/waste adherence, it must be noted that no resin bid comes off after breakage, even if the section surface is being scratched.

Furthermore, on one of the test probes, a few resin bids have even broken on the fracture section: their adherence to the matrix can be considered as comparable to the resin bids resistance.

D) Water effects through immersion:

SYNCRETE cylindric test probes (H. 5 cm, Ø = 4.5 cm, S=102.5 cm^2, V=79.5) have been made by including boron saturated spent ion exchange resins. To stimulate lixiviation tests penalizing conditions, an emulsion with a 25% Cesium chloride saturated water (1.62 kg Cs Cl/1 or 1.27 Kg Cs/1) has been made. The obtained SYNCRETE test probes each contained 22.6 g. Cs (e.g. 285 Kg/m^3).

It must be noted that this Cesium concentration is a lot higher then the one which can be found in standard radwastes; furthermore, in operating conditions, this Cesium had a free ionic form, not linted to the resin bids as it is the case with radioactive wastes. Moreover, the test probes have been immersed immediately after the setting, that is, after 1 to 2 hours. The tests conditions were very penalizing, comparing to that of standard active tests, with a factor at first difficult to quantify, but they enabled the obtaining of a trend of SYNCRETE behavior as regards to lixiviation.

Two lots of seven test probes have been made, each test probe being immersed into 1 L water, so as to analyse within 2 days, 5 days, 7 days, 28 days, 52 days and 90 days since the Cesium release (this last value has not been analyzed up to this date).

On none of the test tubes has there been noticed a measurable variation of the visual aspect, of the external dimensions or of the weight.

After 90 days, the surface state remains qualitatively the same as that of the initial cylinder.

A theoretic calculation of the lixiviation speed after 52 days, gives the following value:

$$RL = 6x10^{-5} \text{ cm/day}$$

This value (after 52 days) is very encouraging for a real test of lixiviation, compared to the known values for other encapsulating matrixes, and this in spite of the tests stringent conditions.

The RL average values obtained when taking into account the 2 tests series are as follows:

Total Immersion during (days)	2	7	14	24	52	104	142
Resistance to lixiviation (10^4 cm/day)	12.1	3.4	1.6	1.2	1.1	0.6	0.6

<u>Tendancy in Accordance with the Considered Application</u>

Looking at the previous results, it seems that the interest in SYNCRETE is mainly due to:

- its good mechanical and impermeability characteristics which should give it an excellent lixiviation resistance.
- its good resistance to radiations, its good resistance to fire, the excellent confinement that it enables to achieve, which allow to think of using it for the conditioning of α and $\beta\gamma$ low and medium activity radioactive wastes.

The first measured characteristics allow consideration of the characterization tests to be undertaken on each waste type with optimism, on one hand in hot conditions, from scale 1 blocks (hot and cold) and on the other hand in accordance with the technology which will be defined for its practical application.

APPLICATION TO THE BULK WASTE EVACUATION PROJECT, AND THEIR CONDITIONING IN A CENTRALIZED UNIT

<u>Aim of This Project</u>

The aim is to evacuate in bulk, spent ion exchange resins, evaporation concentrates, cartrides filters for their further conditioning in a centralized site; this transportation being carried out with a recoverable biological shielding.

In ideal conditions, the utility plant would be then relieved from any processing and waste evacuating problem at very interesting economical conditions.

The first major constraint which conditions the whole of the operations from a technical point of view, consists in the transport regulation, since this constraint implies other technics and economics as regards the whole of the operations.

Especially because of the more or less important quantity of water contained in each waste category, the transportation of wastes as they stand, would be performed under very constraining conditions with very expensive containers.

Waste transportation as it is carried out at present, has the advantage of enabling the transportation groups.

Then, type B packagings are necessary for wastes containing water requires consideration of the study, taking into account the fire test (800°C during 30 mm) with which the packaging must comply in order to avoid important suppressions which involve non-allowed releases by the regulation.

The solution which would consist of a pre-treatment of wastes within the plant, so as to eliminate water and make transport economically feasible, would imply the following consequences:

- A pretreatment operation within the plant would go against the initial purpose, which is as mentioned above, to releave the Utility from the waste processing problems,
- The pretreatment process is to be considered, the cost of the unit itself might bring supplementary expenses, thus burdening in a very significant way the global cost of in bulk disposal.
- The technical feasibility of forecasted encapsulated processes within the centralized plant may be reconsidered by a pretreatment since even if it is optimized as regards further encapsulation, it will not necessarily take into account all the encapsulating constraints.

SYNCRETE utilization, as part of this project, can bring an original solution which involves a continuous and economical process.

SYNCRETE Utilization

The suggested system can be an answer to the question of in bulk waste transportation, (IER, sludges, concentrates) towards a centralized unit.

Effectively, without any discontinuity in the process, the following stages can be performed.

On the waste producer site:

The realization of a thixotropic and stable emulsion of the effluent with a SYNCRETE polymer mixture; this is achieved with a small mobile-unit which is composed of:

- a polymer storage tank,
- a stabilizer and thoxothropic agent storage tank,
- a pumping and emulsifying system,
- an independent tank containing the hot emulsion and its optimized biological shielding.

During transportation:

In the event of a tank fall with watertightness rupture, the emulsion thixotropic character will avoid an important spreading on the ground.

In the event of fire, the emulsion polymerizes spontaneously at a temperature lower than 100°C (60 to 85), which implies a weak vapor release and, therefore, limits the pressure increase in the tank.

On arrival at the processing plant:

The tank is being agitated; it fluidifies the emulsion which is then standardly mixed to SYNCRETE dry matters.

In this respect, a patent request has been registered together by SYNCRETE and STMI.

Technical Characteristics

When the initial polymer is under the form of a 5% water preemulsion, it has a viscosity of a few hundred centipoise and a density of 1.1.

Since the product has been pre-emulsified, its toxicity is very low and its resistance to fire very good: 63°C flash point, 515°C self ignition for a hard polymer, spontaneous polymerization start at a temperature higher than 60°C.

Also two stabilizing agents and one thixotropy agent are being added.

The density of the product transported varies in accordance with the effluent or incorporated waste, but remains in the order of 1.1.

This polymer/waste mixture looks like an unctuous cream which becomes liquid on agitating or on a continuous specific vibration frequency.

The so-obtained emulsion remains stable from -25°C to more than 40°C. Above 60°C, the product polymerizes without gas release or weight loss.

After it has been mixed with cement on the centralized site, the final product will be a cement and polymer concrete the qualities of which depend on the effluent water content and its processing, but the average magnitude will be that described earlier.

APPLICATION TO WASTES CONDITIONING IN A MOBILE ENCAPSULATING UNIT AT POWER PLANTS

SYNCRETE practical application within a mobile encapsulating unit for the conditioning of standard (SIER, concentrates, sludges) or particular wastes does not seem a priori to give rise to major technological problems.

This unit would include the following functional parts:

- pre-emulsioned polymer storage,
- cement storage,
- catalyzer storage,
- emulsifying device,
- mixing block.

The mixing can be made in the final container either by a system of consumable blade driven by a motor, either by predefined oscillations on a containers turning support which has been equipped with internal fixed blades.

In the latter case, the tank can be delivered on site filled up with dry substances (cement + catalyser) in predetermined quantities.

Another possibility for the design of this mobile unit is the setting up of a similar system to that of the COMET units through first preparation of a

SYNCRETE grouting and waste impregnation. To realize this impregnation, the SYNCRETE grouting as mentioned earlier would be used. However, this processing requires a more thorough study, and complementary feasibility tests.

The final block coming out of these machines would have the properties described earlier.

Its conditioning can be carried out either in irradiating packages which are transported with recoverable shieldings or with biological shieldings which ensure a compatible dose rate with the transport regulations and the outside disposal conditions.

In any case, the unit produces a final block directly dischargeable towards a disposable site, an hour after encapsulation at the latest.