PEC ENGINEERING'S WASTE SOLIDIFICATION PROCESS

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ABSTRACT

The new concept for waste embedding plant, should accept either solid wastes from incinerator or dryer and liquid wastes in case of volume reduction plant failure or even maintenance.

The first step in volume reduction, is to feed as much wastes as possible per container, getting a final quality product in accordance with the regulations.

To reach the necessary regulations requirements, an extensive formulation research programm is needed to define the behaviour of each waste as well as additives.

The high filling grade may be obtained by equipment development such as mixing equipment (anti-vortex control head - continuous mixer) and dewatering equipment.

BACKGROUND

Low level waste solidification, specially with hydraulic binder, is a complex and difficult process.

In France, EDF has choosen, since 1974, to solidify the Nuclear Power stations wastes with cement, using PEC Engineering solidification process.

The cement setting phenomena, in conjunction with the chemicals contained in the Radwastes, may sometimes be accelerated and sometimes, not take place due to inhibition.

Our studies have been developped to control such processes and to give to our customer, a process satisfying to French Regulation for waste quality.

In addition to some specific formulations, we have gained a philosophy, to try to solve the solidification problems based on cement setting observations.

In 1982, the French regulation became stronger, PEC Engineering started a qualification programm, still running today, for ion exchange resins solidification, using the DOW CHEMICAL binder.

A mobile system, based on an obtained pre-qualification, has been started to manufacture in October 1983 and will be ready for final qualification on September 1984.

FORMULATIONS

The formulation study has been started to try to fullfil the French specifications, requesting for example, for cement a mechanical strength over 3.000 psi after 90 days, and an equivalent leach index of 10 for Cesium 137 and for Cobalt 60.

The matrix selection has been made in order to reach the specifications.

An extensive formulation research programm has now given us the possibility for several wastes to bind the solidified product specifications, such as mechanical strength, shrinkage or swelling, leaching rate, ..., with at one side, the matrix definition, at the other side, the formulation (embedding ratio, additives, ...).

With the formulations defined, the equipment to process such products have been developped.

CEMENT SETTING FOR BORIC ACID WASTE

Cement setting as discussed in many publications is, when boric acid or borates or others impureties are present, a very complex problem.

Our research programm, based on observations of the phenomena has given us the ability to control it.

Some examples of reactions, and tests are given hereafter.

The cement setting time according to Ca $(OH)_2$ quantity has been determined. An example is given in table I for boric acid waste.

TABLE I
CEMENT SETTING TIME-PORTLAND CEMENT
(H_3BO_3 = 240 gr/l-pH = 8,5)

$\frac{Ca\ (OH)_2}{H_3BO_3}$	SETTING TIME (hr)
0.50	384
0.60	216
0.74	24
0.89	5

The cement setting time is also a function of the cement quality. The table 2 is giving the setting time for different cement quality and for a boric acid waste.

TABLE II

CEMENT SETTING TIME vs CEMENT QUALITY

(H_3BO_3 - 240 gr/l - PH = 8,5 - Ca $(OH)_2/H_3BO_3$ = 0,60)

CEMENT QUALITY	SETTING TIME (hr)
Portland cement type 1	112
type 2	112
Slag cement	672

The reaction time between borate wastes and Ca $(OH)_2$ is very important. Some tests have shown that a minimum reaction time is needed to get a good setting ; this time is shorter if the Ca $(OH)_2$ quantity is higher.

The table III gives for boric acid wastes the setting time according to the reaction time between boric acid and Ca $(OH)_2$.

TABLE III

SOLIDIFICATION TIME vs REACTION TIME

(Boric acid wastes = 240gr/l - Ca $(OH)_2/H_3BO_3$ = 0,72)

REACTION TIME (h)	SOLIDIFICATION TIME (hr)
1/2	72 h
1	48
2	48
3	5
4	5

EMBEDDING RATIOS FOR BORIC ACID WASTES

The embedding ratio is a function of four parameters :

- the boric acid content
- the ratio Ca $(OH)_2/H_3BO_3$
- the addition of some additives
- the cement quality

The table IV gives the water to cement ratio (W/C) for different types of cement and several Ca $(OH)_2$/cement ratios.

TABLE IV

WATER/CEMENT RATIO vs CEMENT TYPE AND Ca$(OH)_2$/ CEMENT RATIO (weight)

CEMENT TYPE	W/C	
	Ca $(OH)_2$ / cement	
	0 %	20 %
Portland cement 1	0.357	0.55
Slag cement	0.347	0.53
Portland cement 2	0.368	0.57
Pouzolanic/cement	0.360	0.55

The Ca $(OH)_2$ increases the water needed for the mixing.

This quantity can still be increased by use of some specific reagents as shown in table V.

TABLE V

WATER/CEMENT RATIO vs REAGENT TYPE

(PORTLAND CEMENT - Ca $(HO)_2$/CEMENT = 20 %)

REAGENT	W/C
VERMICULITE 1	1.40
2	1.52
CECASIL	1.35
REAGENT A	1.21

IMPURITIES

The tables given above are valid for pure boric acid wastes, what happens very rarely. The slurry may contain products like :

- Decontamination solution
- Detergents from laundry wastes
- Anti-foaming agent

Each of these products will change the setting time or the W/C ratio.

A good observation of the problems as they occurs can generally show the means to solve the problems.

Properties

The ability to change different properties of the monolith such as :

- Mechanical strength
- Immersion resistance
- Fire resistance
- Leach rate

have been examined.

The leach rate can be modified by adding some specific reagents. This addition is useful for radio-isotopes like Cs ^{137}.

The table VI is an example of leach rate improvement for boric acid wastes and decontaminations solutions.

TABLE VI

LEACH RATE x 10^{-3} (cm d^{-1})

(Cs 137)

PRODUCTS		BORIC ACID WASTES		DECONTAMINATION SOLUTIONS	
ADDITIVES		NO	YES	NO	YES
Days	2	1.030	0.09	20.8	0.6
	7	0.50	0.06	6.4	0.2
	14	0.37	0.05	2.7	0.1
	21	0.23	0.03	1.2	0.05
	52	0.12	0.02	0.5	0.02
	90	-	-	0.2	0.003

As shown in table VI, the use of some additives, even in small quantities, can improve the leach rate of a factor of almost 100.

The same study has been done for ion exchange resins solidification with cement.

The table VII summarizez some of the results obtained with ion exchange resins.

TABLE VII
ION EXCHANGE RESINS - SOLIDIFICATION WITH CEMENT
(BEADS RESINS - MIXED BEDS)

CIRCUIT	STEAM GENERATOR BLOWDOWN (APG)	CHEMICAL & VOLUME CONTROL SYSTEM (RCV)
Embedding ratio (% W)	23	23
Swelling	No	No
Setting time (hr)	15 - 24	24
Mechanical strength (psi)	2150	1570
Leach rate Cs^{137} after 90 days ($cm\ d^{-1}$)	0.0015	0.001

A similar study for all the waste types has been startes, for waste solidification with the DOW CHEMICAL Binder. These test will lead to a qualification with full size container.

EQUIPMENT

The development has been based on embedding ratios, on formulation studies, on the filling grade and on the process control programm.

MIXING EQUIPMENT

After experiences on both in-drum mixer & continuous mixer, PEC Engineering has tried to improve the in-drum mixer, because the elimination of flushing

The system has been designed to be as flexible as possible, suitable for liquids or solids embedding with either cement or polymer without modifications.

The two main parts of the mixing head are :

1. A drive mechanism and hood.
2. A vortex control plate.

As shown on the sketch below, the Vortex control panel can be part of the mixing head itself (Fig. 1B) or can be the drum lid (Fig. 1A).

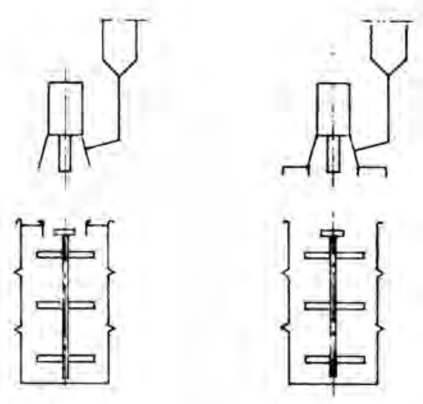

Fig 1a Fig 1b

FIG 1. - VORTEX CONTROL PLATE

The drive mechanism is an high-torque hydraulic motor, which allows a speed variation from zero to 400 rpm, at constant torque, providing the mixing efficiency and the flexibility.

The large speed variation, gives the possibility to process liquid or solid wastes and to use cement or polymer without modification on the driving mechanism.

The hydraulic power pack can be located outside the radio-active area, decreasing as much as possible the mechanical parts in contamined rooms.

The mixing, using an in-drum container mixer, produces a Vortex which, without specific protection, will limit the filling ratio as shown in Fig. 2. Without Vortex control plate the normal filling ratio is typically 80 %.

The purpose of the vortex control plate is to prevent the overflow due to the Vortex, and to push the fluids back down in the center of the drum. The product flows is shown on sketch Fig. 2.

No Vortex control plate With Vortexcontrol plate

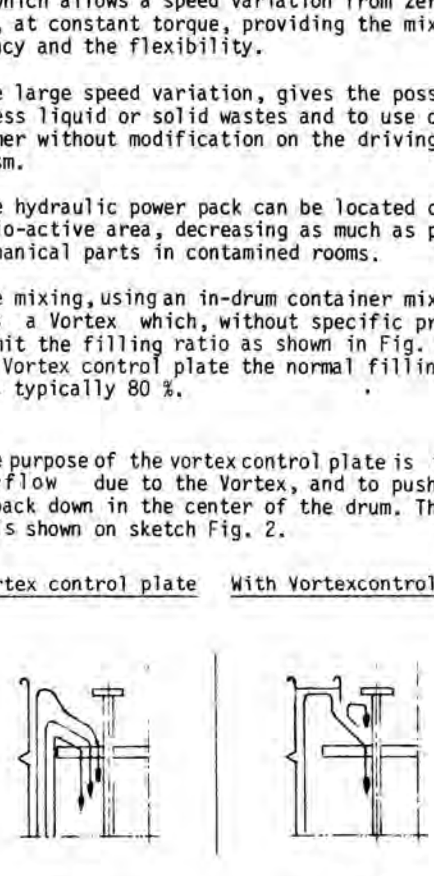

Fig 2a Fig 2b

FIG 2. - MIXING MOVES

The effect of these controlled flow, in conjunction with the drive mechanism, is to increase the mixing efficiency as well as the filling ratio.

The best results are obtained with specific mixer design according to the viscosity of the product.

The filling ratio can be increased up to 90 % and often to 95 % with Vortex control plate.

The Vortex control plate is also providing splashing safeguards, providing clean lids after mixing, and no drum walls contamination.

ION EXCHANGE DEWATERING UNIT

To increase the embedding ratios and simplify the solidification, it is desirable to dewater ion exchange resins prior to solidification.

The PEC Engineering ion exchange dewatering unit is based on a special solid feeder with metering screws self cleaning, and a bridge breaker to prevent bridging in the hopper.

The equipment has been modified by adding a screen in the bottom to dewater the ion exchange resins by means of a diaphragm pump.

When the ion exchange resins are dewatered, it is also possible to dry them, with hot air. The free water content can be kept down as low as requested.

This equipment can be used for dewatering before embedding with cement as well as for dewatering for storage is HIC.

The quipment space requirements are quite low and can be installed in small room.

PEC Engineering is manufacturing a mobile embedding system in which such dewatering equipment is installed.

CONCLUSIONS

Under the pressure of stronger and stronger regulations requirements, PEC Engineering has gained significant experience and expertise in radwaste solidification with cement or polymer.

This expertise is available today from PEC Engineering or KOCH Process Systems, INC for us applications, regarding waste solidification formulation as well as plant equipment modifications.

The equipment have been developed for the main purpose of plant retrofit, to replace non operating systems, to fulfill new regulations, to decrease the investment costs, as well as reducing the down time to as low as possible.