The Vitrification as Pathway for Long Life Organic Waste Treatment

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ABSTRACT

Worldwide, several vitrification processes have been developed and are industrially exploited for the vitrification of high level waste, attesting the efficiency of this technique for fission product treatment and glassy materials for nuclear waste containment is the conditioning that receives the best acceptance. However, these processes operate a very high technology and strangely, for less radioactive waste such as long live intermediate level waste, this technology did not break through even when their final disposal scenario are very close (except mainly thermal consideration).

This reflexion gives example for anyone to appreciate how the vitrification of organics intermediate level waste can be an excellent solution and even a competitive technical-economic answer with limited industrial risks.

By "vitrification of organics", we mean in this paper the incineration/vitrification of mixed organic and mineral waste; this results in gasification of organic matter and vitrification of the oxidized mineral fraction of the waste. Such processes can accommodate any ratio of mineral/organic from pure burnable waste to pure mineral sludges. Many advantages come with the vitrification of organics: Treatment of the organic matter, gas release avoided, existing suitable glass composition families, and volume reduction.

The technological characteristics that should show a vitrification process for organic waste according to our experience in this field is detailed and examples of treatment with chlorinated waste or old bituminous drums reprocessing are given.

INTRODUCTION: THE ADVANTAGES OF A VITRIFIED WASTE

The main advantage of the vitrification technology applied to organic waste, and definitely the one that could be the mainspring of such a choice is the volume reduction of the final package. Considering that geological disposal costs will be high per cubic meter, huge savings are possible even with a small volume reduction factor; we give further in this paper several examples of volume reduction from 2 to 50. Of course, this is true only if we discuss about packages designate for geological disposal, where costs per cubic meter relegates background an investment for a treatment shop. This is not true in the case of low level waste for which disposal cost does not balance the cost of a vitrification treatment shop. If we look at the studies that have been carried out worldwide in the field of vitrification of organic waste, we can observe that, excepted few examples, it is mainly for low level waste that processes has been developed [1], resulting in almost no industrial achievement (excepting the Swiss ZWILAG facility). This can

be one of the reasons why the vitrification of organics did not break through. Maybe we have to consider that this technology is to reserve for waste where the potential benefits are really more important than the industrial risk induced in building and operating a new treatment shop; intermediate level waste with long life radio nuclides match this requirement.

But volume reduction is not the only benefit of the vitrification process for organic waste. The organic matter is destroyed and the final waste product is a glass. This means that you only have to deal with the organic once during the process treatment and not for the storage.

In the same idea, waste radiolysis is not any more an issue for storage or disposal as it can be a real concern in some cases. The gas release problem in storage from package is solved.

In the case of potentially corrosive compounds in the waste, the corrosion problem is treated during the vitrification process and is not perdurable during storage. The case of highly chlorinated waste is of interest and is developed in the paper.

We can also add, as it is exposed in this paper, that glass formulation can be adapted to a wide range of waste composition and can rely on dozens of years of research. Various glass formulations have been demonstrated to be perfectly adapted to diverse organic waste families.

CHARACTERISTICS OF AN ORGANIC LONG LIVE WASTE VITRIFICATION PROCESS

The following discussion is based on the postulate that the vitrification process for organic waste is devoted to intermediate level waste. Such facility will have to operate in a hot cell, that's why it should comply with these requirements:

1. A limited number of apparatus.
2. As compact as possible.
3. A minimum amount of gas flow rates.
4. A minimum generation of secondary waste.
5. Aggressive corrosion resistance.

To limit the number of apparatus, the goal is to achieve in the same reactor the incineration of the waste, the vitrification of the mineral fraction and the complete combustion of the gases. Succeeding in making these three actions with only the heart of the process is the key to a compact process. The size of the equipment in high temperature processes is directly proportional to the gas flow rates. This is why the elimination of a secondary burning chamber for the gases combustion gives a real advantage in term of size: there is no addition of extra air for this purpose that has to be cooled down, filtered and washed. But of course this assumes that the combustion is complete at the exhaust of the vitrification reactor. The plasma technology is a good tool to comply with these points, because pure oxygen can be used and combustion performances are high.

The organic waste comes commonly with a very variable chemical composition but also with elements that can generate very corrosive gases or solid compounds: Chloride, sulfur, and fluorine. In many cases, refractory furnaces won't meet the requirement of low secondary waste

(lifetime too short) and will induce a high frequency maintenance and put a strain on the facility operation. The metallic cold crucible is a technology that gives answer to these requirements.

EXAMPLE OF THE SHIVA PROCESS DEVELOPED BY CEA

The SHIVA process (Advanced Hybrid System for Incineration and Vitrification) is the technology that CEA is developing for the organic long live waste treatment. The furnace is a stainless steel double-wall unit cooled by pressurized water; it is 60 cm in diameter, 50 cm high with 20 cm for crucible depth, it contains up to 100 kg of glass. Anode and cathode of the cold-wall plasma combustion / vitrification melter are aerial metallic electrodes (see Fig. 1).

The twin-torch transferred arc system includes two plasma torches of opposite polarity. For each torch, two water-cooled nozzles are used to feed argon and oxygen in the plasma, respectively to shroud the electrode and as reactive plasma forming gas. A spherical bearing arrangement allows variation of the angle between the torches and the inter-electrode gap. Arc intensity is from 150 to 300 A; distance between the tungsten cathode tip and the copper anode end is from 5 to 10 cm as well as between electrode tips and the melt surface. Plasma forming gas flow-rate is in the range of 20 to 200 NL/min for each torch.

The direct inductive heating system consists of a double coils flat bottom inductor, placed under the crucible. The crucible bottom is made to be transparent to electromagnetic field. The operating frequency is around 280 kHz and the electrical power 200 kW.

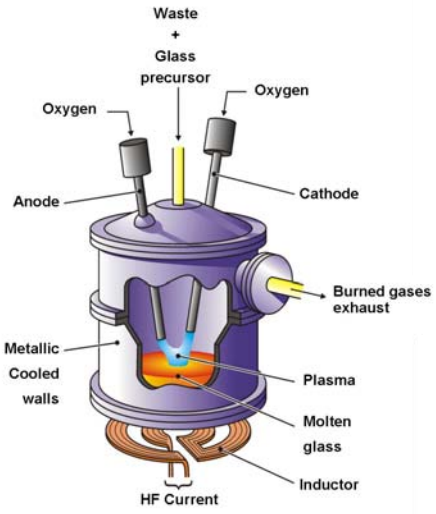

Fig. 1. SHIVA: Advanced Incineration / Vitrification Hybrid System.

Off-gases are sent to a suitable treatment system including two filters (Electrostatic tubular pre-filter and bags filter), a wet scrubber (water and soda) and a fan.

The complete process is very compact; its ground surface is less than 20 m².

EXAMPLE OF CHLORINATED WASTE TREATMENT

An interesting example of vitrification of intermediate level waste containing long life radionuclides is the case of the technological waste containing a high fraction of chlorine. Such waste are for example produced in shops where alpha emitters are manipulated in glove box: MOX fuel fabrication, weapon dismantling, end of reprocessing plant, … These wastes are composed of cellulose, rubber, neoprene, polyethylene and of course PVC providing the high amount of chlorine [2]. Table I. gives the example of an elementary composition of such waste. It can be seen that chloride is upper to 20 w% in the same time as mineral compounds are in the order of 2 w%. The main mineral compound, coming from neoprene or rubber additives is zinc. In the thermal treatment temperature and residence time conditions, zinc and chloride form a highly hygroscopic, corrosive and volatile compound: the zinc chloride.

Table I. Chlorinated Technological Waste Elementary Composition (mean composition).

Elements	C	H	N	O	Cl	S	K	Ca	Zn	Al	P	Others
w%	57.9	7.8	0.3	9.3	22.2	0.4	0.1	0.2	0.6	0.2	0.6	0.7

It has been shown in previous studies [3], that it is possible to substitute the chloride compound of zinc by a phosphate compound if organic phosphorus is added at the proper temperature with the adequate residence time. These studies also determine that this phosphatation reaction is a gas phase reaction that needs a high gas temperature.

As well known, it is impossible to incorporate in the glass the chlorides compounds. Their transformation into a phosphate compound is a challenge to incorporate all the mineral fraction of chlorinated wastes in the glass.

Tests have been performed with the SHIVA process. The strategy adopted in this case was to incinerate the waste on the glass surface while performing the phosphatation of chlorinated minerals in the plenum thanks to the plasma temperature and recycle in the glass the dusts recovered in the filter as phosphates. The tests performed demonstrate this feasibility. Table II. gives the composition of the dusts recovering from the filter; it can be seen that minerals are partially in the phosphate form but also that some chlorides remain. It must be said here that all the phosphorus as reacted during the treatment and this chloride remaining in dusts is mainly due to under stoichiometric phosphorus conditions.

Table II. Dust Composition for Highly Chlorinated Waste Vitrification (w%)

Element	C	Cl	S	P	Na	K	Mg	Ca	Zn	Al	Si	Sb	Ni	Fe	Cr	Ba	B	O
Filter dusts	1	26	0.62	11.5	9.5	3.25	0.25	1.25	20	1.9	1.9	1.5	0.1	1.1	0.15	0.25	3.1	15.7

These dusts have been further vitrified at laboratory scale with glass additives to show the possibility to recycle them in the process. The vitrification of technological chlorinated waste

represents in the case presented here a volume reduction factor of 57 from bulk waste. This volume reduction factor is between 5 and 6 if we consider the comparison of the glass package versus the compacted waste package.

EXAMPLE OF OLD BITUMINOUS WASTE

Another interesting application of the process presented here is the reprocessing of old waste that has been stored and must be repacked for future final disposal. Such storage cost will be very expensive and a vitrification treatment could lead to a volume reduction of the final wastes compare to a simple over drum (that increases volume) and dramatically diminish the storage cost.
For this study, two different typical bituminous packages have been defined to represent the major part of the existing drums (see Table III.) and added with radionuclides surrogates (with an amount compatible for analysis). The test reported here concerns incineration / vitrification of a main composition bituminous media.

Table III. Bituminous Package Reference Compositions for Vitrification Studies (w%)

	Main composition	Secondary composition
$Ca_3(PO_4)_2$		9.0
$BaSO_4$	13.9	
$Fe(OH)_3$	8.2	6.3
$Ni_2Fe(CN)_6$	4.5	4.0
Coal	1.9	2.0
$Cu(OH)_2$	1.9	1.0
$Ni(OH)_2$		1.2
MnO_2	0.4	0.3
Na_2SO_4	0.5	1.0
$NaNO_3$	1.9	0.2
$Ca(OH)_2$		6.0
Diatoms	4.0	4.0
TBP		3.0
Tensioactive	2.0	2.0
Eau	1.0	
Bitume	60.0	60.0
Total	100.0	100.0

The crucible is initially filled with 35 kg of borosilicate glass frit (see Table IV.). The plasma is first used to start the melting of the glass frit and after about 45 minutes, the HF power for glass melting is started and held around 120 kW. After complete melting, the torches are moved back from the bath surface to avoid high volatilization and the HF power is decreased between 45 and 75 kW in order to maintain the temperature of the molten glass around 1300 °C.

Table IV. Glass Frit Composition (w%)

SiO_2	B_2O_3	Na_2O	Li_2O	CaO	Fe_2O_3	Al_2O_3	ZnO
58.0	16.4	10.8	1.2	2.4	2.2	7.2	1.5

The waste is processed by feeding in the furnace, on the glass surface, through a channel. As the plasma columns radiation is very important, the bitumen ignites as soon as introduced in the furnace and burns in the oxidizing atmosphere. During the waste treatment, the plasma power is 50 kW (220 V, 230 A), with 90 Nl/min of argon and 190 Nl/min of oxygen. 40 kg of waste are treated in 8 hours (mean feeding rate of 5 kg/h). The oxygen excess is 75 % (190 Nl/min are fed for a stoichiometric demand of 107.5 Nl/min). The extra power supplied by the bitumen combustion is 32 kW in these conditions.

After the test, all the facility components are carefully cleaned in order to collect the residues. About 45 kg of glass have been produced. A small amount (300 g) of non-integrated waste, partially reacted with glass, is recovered on the surface of the glass, near the wall of the crucible, under the feeding channel. Some Fe, Ni, Cu and S balls are present in the bottom of the crucible.

The dust partition is as follows: furnace wall: 520 g, furnace exhaust: 200 g, filter 1: 61g, filter 2: 545 g. This represents 2.01 w% of the treated waste, or 2.58 g/Nm^3 in the exhaust gases. This is a common reasonable value of dust in such high temperature process.

Chemical analyses are performed on samples to produce the glass composition (see Table V.). From Table V., it is interesting to focus on the barium content in the produced glass because it is a good indicator of the waste mineral phase integration into the glass. The 6.1 w% in the glass represents 84% of the introduced barium. From dust partition and analysis, we also can calculate that 1.1 w% are on the inside walls of the furnace, 2.1 w% are in the accumulation on the surface and 0.5 w% in the filter dust. 89 % of the introduced Ba is recovered; this is a good value if taking into account all the possible errors. This Ba mass balance teaches us a very good integration of the oxidized salts in the glass. We also can see from this analysis, some signs of elements reduction: copper, nickel and iron. Copper and iron are gathered partially in rich phases in the glass or in a small amount of metallic phase.

Table V. Glass Composition (w%) for Major Species (theo. > 1%). Analysis is given with ± 10% for Values > 5 % and ± 50 % for others

	Recovered glass	Theoritical glass
SiO_2	53.4	47.1
Na_2O	10.2	8.9
B_2O_3	12.2	12.3
Al_2O_3	6.1	5.9
BaO	6.1	7.3
Fe_2O_3	4.8	7.9
CaO	2.2	1.8
ZnO	0.6	1.1
CuO	0.1	1.3
NiO	ND	1.8

The partition of the elements in the facility, other than glass, is also studied thanks to chemical analysis of samples. It can be observed for example that, without dust recycling, 26.6 % of the cesium leaves the melter (73.4 % are shared in the glass, accumulation and internal walls). The volatility of zinc, coming from the glass frit is also visible and is probably due to the transformation of the zinc oxide in the reduced metallic form. Other waste constitutive elements

have a good integration, considering there is no dust recycling. Volatile elements are easily recyclable in the reactor with an adapted dust management, as it has been proven with laboratory tests only at this moment.

In term of volume reduction, the volume reduction of the waste is ~ 1.9 for this test. This gives a 3.8 reduction factor by comparison to a "over drum" solution in 400 liters drum. A simple technical / economical study has shown that the cost saving can be up to a factor of 3, considering investment, treatment and disposal cost.

CONCLUSION

Based on two examples that have been studied in the CEA's laboratories, we show in this paper the possibility to apply with good technical and economical confidence a vitrification treatment for organic waste. Other kinds of wastes have been tested with success: ion exchange resins with high mineral load [4], sulfate slurries, graphitic sludges.

We postulate that the vitrification technology for organic waste is of interest mainly in the case of intermediate level waste because the profit coming from the volume reduction for final disposal can largely balance the cost of a treatment shop investment. Other advantages have to be taken into account at the same level: no organic matter in storage, no gas release in storage.

The technology proposed as a vitrification process relies on the large skill developed by the CEA teams based on the cold crucible melter technology developed for more than 20 years but also on the oxygen plasma transferred mode plasma torches that have been tested for more than 10 years.

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