Comparison of Stabilisation/Solidification-treatments of hazardous waste materials

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1. Summary

In this paper the advantages en disadvantages of three different Stabilisation/Solidification-treatments are discussed. The first treatment, cement based S/S-treatment, is based on the hydration reaction of cement by which heavy metals chemically and or physically are bound. Cement based S/S-treatment is more critical with regard to the used waste materials than most of the other S/S-treatments. For that reason, research particularly is directed on the enlargement of the chemical and physical bounding by adding additives. The compressive strength of the material is usually below the compressive strength of concrete, near 5 to 50 MPa. Moreover the materials are sensitive to moisture and fluctuation in temperature which can result in the formation of cracks.

The second treatment is based on the addition of organic binding agents. Bitumen is the most frequently used. In addition experience has been gained with S/S-treatments on the basis of styrene. Organic solidified waste materials show a slight leaching of components that mainly are implied physically. The materials show a high grade of impermeability in comparison with cement based solidified waste materials. Through this, not many requirements are set for the waste material. The compressive strength of the material is near 15 to 100 MPa. The materials are insensitive with regard to external influences. An exception comprises the presence of oxygen and UV radiation. The expenses, related to S/S-treatments with organic binders, are significantly higher than these of cement based stabilized waste materials. An aspect concerning the environmental benefit is possibly a waste-to-waste approach. Harmful influences for the environment are the emission of volatile components and the consumption of energy.

The third treatment is thermal S/S-treatment of waste materials. This technique falls into three groups: sintering, glazing and crystallisation. The difference with the three preceeding techniques is that the waste material is transferred into a crystalline, amorphous or ceramic material by raising the temperature. For the sintering, producing a ceramic material, a temperature between 800°C and 1150°C is required. Crystallisation and glazing takes place at melting temperature, approximately 1450°C. Gradual cooling of the melt at a temperature between 800°C and 1400°C provides an crystalline material whereas a rapid cooling provides a amorphous material. The leaching behaviour of the three materials is mostly favourable compared to the other two treatments. Little requirements are set for the waste material, but a high content of oxides and silicates is favourable. The stability of the products under the influence of external influences is reasonable. Possibilities of utilisation therefore are rather big. Expenses are between $75 and $350 per ton product depending

on the possibilities of regenerating energy from the waste material. The high consumption of energy and the possibly created flue gas is, in certain cases, environmentally harmful.

In general, there is a lot of uncertainty about the actual quality of S/S-waste materials. Some adequate information and an assessment method is missing. In addition, an assessment tool for the long term release of components due to application conditions is desired. Therefore, more research is needed towards the long term behaviour of the different S/S-waste materials. Because dumping capacity is more and more a problem, carefully controlled application of these materials in practice should be stimulated.

2.   Opening remarks

Extensive examinations concerning Stabilisation/Solidification treatment (S/S-treatment) of hazardous waste materials have been performed world-wide, in order to contribute to less use of scarce space. S/S-treatment might be beneficial for waste materials that have to be tipped costly with the necessary isolation, management and control facilities. The target that has to be set is to change waste materials as such, physically and chemically, that the risk of dispersal of environmental pollution through leaching, erosion and dispersion on the short and long term will decrease. Remnants that have to be considered are hazardous waste materials, due to their leaching behaviour. The remnants have to be a substantial part of the solidified waste material in relation to the additives and binders. For example, incineration fly ash is occasionally used as filler in asphalt. However, due to the low percentage of fly ash used, this processing of waste materials does not count as S/S-treatment. Particularly, cement-based S/S-treatments, S/S-treatments on the basis of bitumen and melt down has been studied. To a lesser extent, research has been performed on sintering of waste materials.

S/S-treatments aim at reducing the release of hazardous components by adding a binder or changing the molecular structure of the waste material. Three methods under investigation are: adding cement, adding an organic binder and thermal treatment. The Stabilised/Solidified waste material may be usefully applied or disposed of. In this paper, the three treatments are compared with respect to leaching behaviour, used additives, required characteristics of the waste material, degradation mechanisms, methods of application, expenses and environmental aspects. While S/S-treatments often show good performance on leaching and application possibilities, only a few application are known. The comparison made in this paper is aimed at supporting decision makers in effective implementation of S/S-treatments.

In Japan, the United States of America and France, research on S/S-treatment has been in progress for quite a while and some techniques have been put into practice. S/S-treatment of hazardous waste materials became relevant as the amount of hazardous waste materials is increasing on the one hand, and the number of the disposal sites is decreasing on the other hand. In countries like Denmark, space is a minor problem, whereas in Japan the shortage of dumping capacity is a significant motive for S/S-treatment.

At present uncertainty about application possibilities exists among research workers and possible customers, caused by the obscurity of the Stabilised/Solidified-waste material, the legislation and

the negative image. Due to uncertainty, this implementation of S/S-treatments is risky for investigators as well as for customers. A solidified waste material of high constructive environmental quality runs the risk not to be accepted. More and adequate information directed at possible costumers, investors and legislators may enhance the acceptance of stabilised/solidified-waste materials.

3. S/S-treatment on the basis of inorganic binders

S/S-treatments with inorganic binders are generally based on the addition of cement to waste materials. There also has been done some research on S/S-treatment on the basis of sulphur, (Albino, 1996) en (Lin, 1995). Cement based S/S-treatment is brought in practice in several countries like the United States of America and Japan. Solidified waste materials of zinc-ash, polluted ground and purification silt have been applied in trial project on road-foundations. These road-foundations were carried out without isolation, sealed on top with asphalt. Through control of the quality of the surrounding soil, parts of the road foundation with poor quality can possibly be tracked and removed. Likewise, S/S-treatment is brought in practice by blending Municipal Solid Waste Incineration (MSWI-) bottom ashes, filter dust, MSWI flue gas cleaning residues and waste-water with cement.

3.1. S/S-treatments on the basis of cement

S/S-treatments on the basis of cement affiliates to processing properties for manufacturing of concrete. Dehydration of the waste material prior to binding with cement is necessary if the waste material contains more then 50% of neutral water. Blending with additives, see paragraph 3.3, before addition of cement may be necessary for a particular chemical fixation. Therefore the waste material has to be homogenized at first. Subsequently the waste material will be mixed, if needed, with water, cement and eventual additives at room temperature. 20 to 60 weight-percentage of cement is typically added relative to the waste materials. Choice of the cement depends on the desirable pH. After blending a hardening period in a mould follows.

3.2. Leaching

The leaching of components out of Stabilised/Solidified waste materials is controlled by physical and chemical fixation mechanisms. Physical mechanisms depend on hardening and porosity of the material. Because of the fact that the final matrix has a higer compressive strength than the waste material, most of the components will be implied physically. Organic components, salts, volatile components like mercury and oxyanions are generally difficult to immobilise either physically or chemically. Some components from the waste material have a negative influence on the hardening. Particles smaller than approximately 74 mm are weakening the combination between waste materials and cement through forming a layer around the bigger particles (Noyes,1994), which will, next to the defamation of the physical bonding, prevent the chemical bonding of some components. Organic components in the waste material may also result in a weaker product. The presence of oil and fat, for example, weakens the bonding between surcharge materials and cement (Noyes, 1996). Anyhow organic components can be changed, at the high pH, into dissolvable components (CUR, 1993). Soluble salts may cause an increase of the porosity, resulting in lowering strength because of the fact that these components are washed out (CUR, 1993). Chemical mechanisms are the result of

chemical attraction of surface atoms and precipitation of hydroxides. Some heavy metals, like cadmium, can be bounded by the cement matrix by way of adsorption and chemisorption. These components will be taken into the crystalline structure of the cement (Noyes, 1994). Some cations precipitate as hydroxides due to the high pH (see fig. 1). However, most of the cations have lowest solubility at pH of 8 – 10 (Meima, 1998). Above this pH, the pH in (hardened) cement is approximately 13, the solubility is increasing. The solubility of oxyanions like molybdates are, at this pH, high. An advantage is that at pH > 13,5 and the right additives, dioxins will be turned into harmless components. Most of the anions can not be chemically fixed, except sulfates and sulfites.

3.3. Additives

A lot of research has been done on the right additives for S/S-treatment of hazardous waste materials (Means, 1995). The aim of the first category of additives is to improve the physical confinement by optimising the hydration reaction. For that purpose, pozzolanic materials like fly ashes can be added. Pozzolanic materials demand an external calcium source in order to get the reaction going. This external calcium source may be $CaCO_3$, $CaCl_2$, $CaSO_4$. NaOH and MgOH can also be used in order to optimise the reaction of hydration. Calcium aluminate could be added with which salts could react into ettringite. As a result of this an extra confinement of salts and an extra formation of ettringite occur. The second category of additives is added in order to chemically bind inorganic components which, otherwise, would wash out easily. Examples of this are: dissolvable silicates, decelerators, oxidants and inorganic components with which the components, possible to leach, precipitate (CUR, 1993), Noyes, 1994). As dissolvable silicate, water glasses, particularly amphoteric metals ($Na_2Si_4.xH_2O$) are chemically bounded. Disadvantage of this is that the decreasing volume through which cracks could form (Noyes, 1994). Decelerators and oxidants like Fe^{2+}, Fe^{3+}, Mn^{4+} and SO_4^{2-} are added in order to allow salts to precipitate. The REDOX-reactions produce, in these cases, a minor dissolvable salt. An example is the oxidation of Fe(II) to Fe(III) and the reduction of Cr(VI) to Cr(III). Clays are added in order to bind inorganic components to free water. Another, different function of clays is to bind organic components. By that, the third group of additives is introduced, those for leachable organic components. The S/S-treatment of organic components, bound in cement, requests particularly absorbing materials like active coal, clays and polymers. By adding clay, organic components will be bound. The hydroxyl- and carboxyl groups are attracted by the Ca^{2+}-iones. Aromatic, organic compounds can be absorbed by stratified clay. For this purpose, clay is modified with alkyl ammonium. The clay surface no longer has hydrophobic but inorganic characteristics. Another additive is an organic polymer-dispersion. The polymer forms a film inside the pores. Organic components peeling off the matrix are absorbed by these polymers.

3.4 Characteristics of waste materials

Experience has been gained with a number of different waste materials. Waste material of combustion installations provided the following results. Three remnants, MSWI fly ash, filter dust and evaporation residues have been immobilised. Evaporation residues are containing a lot of salts and are, for this reason, not suitable for cement based S/S-treatments. As a filter cake has no pozzolanic action and is lycophillic, other methods of processing are searched for. MSWI fly ash has pozzolanic action and therefore is quite suitable. Filter dust could possibly be used as extra surcharge with

the S/S-treatment of MSWI fly ashes. Desired properties of waste materials are (Means, 1995):

- high contents of metals like lead and cadmium;
- a low organic substance-content because of the required extra additives;
- a low content of bromides, molybdenum, chromium and zinc because of the mobility of these components;
- low contents of volatile components like mercury.

Not only is the chemical composition of importance but the pozzolanic activity too is an important positive characteristic of waste materials.

3.5 Degradation mechanisms

Cement based S/S-treatments are sensitive to various degradation mechanisms, corresponding to those acting on traditional concrete (CUR, 1993). These are: erosion, wet/dry cycle, freeze/thaw cycle and fluctuation of temperature (Whalström, 1991). The sensitivity for erosion depends on the strength of the product. A high strength gives a good resistance against erosion. The presence of wet/dry cycles can cause the product to swell or shrink or can cause leaching of the components. Particularly if clay is used, shrinkage resulting from drying periods can lead to the formation of cracks in the Stabilised/Solidified material. The extent of shrinkage is mainly determined by the water/cement-factor (W/C factor). Shrinkage can lead to cracking of the material. However, the influence of moisture is of less importance with reference to the formation of cracks than frost/thaw cycles. Cement is quite sensitive for frost/thaw cycles. Because of the presence of water inside the pores, which can become frozen during low temperatures, tensions may occur inside the solidified waste material. This can cause micro- and macro-crack formation. A special case of frost/thaw cycles is one with presence of de-icing salts reducing the freezing temperature. The concentration of these salts is, in the core, lower than on the surface. As a consequence of concentration and temperature difference, the core as well as the surface of the solidified waste material are freezing. The isolated water is getting under high pressure which can cause crack formation (El Korchi). If polymers are added to the cement, oxidation of the polymers at the surface may take place. Carbonation of cement also may occur, resulting in a lower pH at the surface of cement. As the mobility of heavy metals at a pH between 8 and 11 is minimal, the S/S-treatment is optimised (see figure 1).
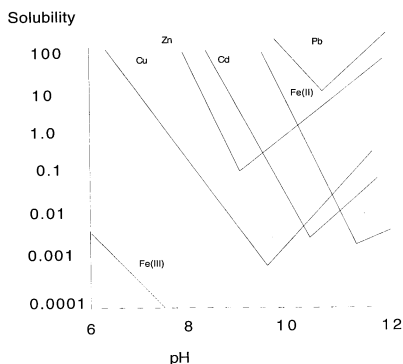

Figure 1. *Typical solubility curve for metals over a range of pH*

3.6 Methods of application

In the Netherlands, the useful application of building materials is limited by the Dutch Building Material Decree (DBMD). This decree sets standards for the leaching of building materials. If the Stabilised/Solidified-waste material is usefully applied, these standards have to be met. Besides that, constructive quality will define the possibilities of application. Leaching behaviour of most products is such (i.e. too large amounts of hazardous components are leaching) that they still have to be dumped (Born, 1996). The compressive strength of the material is less than the one of traditional concrete, between 5 en 50 MPa (Born, 1996), (Rebeiz, 1995), (Technotrans, 1998). Because of deformation mechanisms, the use is limited to materials that are sealed, taking erosion into account and, for materials that are used half a meter above groundwater, taking frost sensitivity into account. Possible applications are replacement of gravel, embankment materials and foundation materials for roads.

3.7 Expenses

The costs of processing waste materials into solidified waste materials are estimated at less than $50 per ton product and $175 per ton product (Born, 1996). Additives particularly determine these costs. Through this the technique is flexible and no major investments that have to be earned back through the years are necessary. A few examples of prices for additives are: Silicates $250 to $500 per ton, the polymer dispersion $750 per ton. These costs can be earned back by the lower volume that has to be dumped. Only limited benefits are expected by sale of the solidified waste materials. Because of the unacquaintance of the solidified waste materials, money probably has to be added in order to apply the product.

3.8 Environmental aspects

The environmental efficiency is negatively influenced by the fact that:

- the primary added additives occasionally are of high-grade;
- in some cases extensive transportation of the waste materials takes place, namely from the waste disposals to the processing companies and to the final destination. Situating the installation for the S/S-treatment next to the combustion installations could restrict this. A mobile S/S-treatment station would also restrict the necessity of transpiration.

An alternative processing of fly ashes and filter dust, mixture of waste materials and water would probably cause more environmental profit; that way a hard mass with smaller volume is created that could be dumped but that would have a favourable leaching behaviour than the separate fly ash.

A positive contribution of the processing is:

- the substitution of raw material; in some case solidified waste materials can replace gravel and founding materials;
- a second positive contribution is: reduction of the leaching of the for the environment harmful components;
- the energy consumption of this technique is extremely low compared to thermal S/S-treatment. However, the energy used for the production of cement is quite high through the high temperatures and also has to be considered;

- in some cases, a decrease of the dumping volume can be realized (along with an increase of weight) as the density of the immobilized waste materials is higher than that of the initial waste materials. That means less occupation of dumping ground.

4. S/S-treatment on basis of organic binders

The experience of S/S-treatment with organic binders is particularly based on bitumen, getting released during the process of oil refinery. Research has been performed concerning in-situ S/S-treatment of zinc-ash with 6%-foamed bitumen. This includes a couple of kilometres of road. MSWI fly ashes are also applied as filling materials in asphalt. The percentage of waste materials in this application yet is little, approximately 2 weight percents. Raising of the content of waste materials is difficult because of exceeding the maximum water and acid solubility of the filling material. Other widely used thermoplastics are: polyisobutylene, polyesters, polyurethane and paraffin (Noyes, 1994). Another organic binder used as stabilisation/solidification-agent is styrene, a thermoset.

4.1 Bitumen

Bitumen is fluid at approximately 140^0C. Depending on the polymer a temperature between the 130^0C and 350^0C will be applied (Noyes, 1994). At this increased temperature the waste material will be pumped, continuously, into the polymer and the water inside the waste material will evaporate. By means of mixing the polymer with waste materials, a homogeneous mass is created. The material can be vibrated in order to let the existing air disappear out of the matrix. The follow-up treatment includes cooling of the mixture causing the development of a hardened material. By doing so, moulded and none moulded products are made.

4.2 Styrene

The S/S-treatment by means of styrene is based on polymerisation of monomers or partly polymerised dispersions of polymer chains. For that purpose, catalysts or UV-radiation are demanded. Possible catalysts are: peroxide in combination with polyesters, polyurethane en polyacrylic. Catalysts not only are necessary in order to get the polymerisation going but also to discourage the evaporation of styrene. Zinc and lead out of the waste material can also act as catalysts. In that case, less additives are required. The polymerisation of monomers usually appears at a low pH (Colombo, 1988). For urea formaldehyde, for example, a pH at about 1.5 is required (Conner, 1990). The process is implemented at room temperature. Polymerisation lasts only for a few minutes and creates a hardened product in which the waste material is locked up. After this process, the polymerisation and therefore the hardening process can go ahead. Granulates and moulded materials are generated.

4.3 Leaching

The S/S-treatments on the basis of polymers is based on a confinement of waste materials in the hard matrix: a meso-confinement. In case of an impermeable layer, a coating will surround the waste material, it is a matter of macro encapsulation. Meso- and macro-encapsulation is possible with both thermoplastics and thermosets. Furthermore, thermoplastics can cause a physical-chemical combination in the form of an physical adhesion of waste materials on the matrix (POSW, 1995),

a micro-encapsulation. Heavy metals might be integrated in a polymer chain in the form of cyanides, carbides or nitrites. No chemical combinations take place between waste materials and polymers. Organic solidified waste materials do have a high impermeability relative to cement based solidified waste materials due to the hydrophobic character of the material itself and the absence of pores. Even if the material would be reduced extensively, it would be reasonably resistant against leaching (Conner, 1990). Leaching of components is particularly caused by erosion of materials on the surface. Thermoplastics are showing an initially increased leaching of easy dissolvable organic components and, in minor extent, of organic components. Volatile components, like mercury, can poorly be Stabilised/Solidified.

4.4   Properties of waste materials

Organic polymerization is applied to a great variety of waste materials containing organic as well as inorganic components. Granulates as well as pulverised waste materials can be stabilised/solidified. In foreign countries, research has especially been performed on radioactive waste materials (Colombo, 1988). Zinc-ash and MSWI bottom ashes have been investigated with regard to S/S-treatment with bitumen. Amongst others grit blaster, riddle sand, breaker sand, fly ashes, residues of drinking water purification, aluminium oxides and polluted soil are Stabilised/Solidified with thermoplastics. In spite of the great use for S/S-treatments with organic binders, a number of the properties of waste materials are working out badly:

- a restriction of S/S-treatments based on thermoplastics is that the components should not degrade at increased temperature (Conner, 1990). This causes fire risk of oxidising components;
- strong oxidants are, likewise, not advisable as these components can crack the matrix through oxidation (POSW, 1990);
- dehydrated salts can be harmful as of rehydration occurs in contact with water (POSW, 1990);
- organic material with a large molecular weight, high steam pressure and hygroscope properties are often leading to an unacceptable product (Noyes, 1994);
- for S/S-treatments on the basis of styrene a dry dust content of more then 92% is desired. At a lower dry dust proportion, the strength of the product is lowered. Therefore, drying of the waste material can be desired (Holman, 1995), (Powers, 1996);
- with thermosets, the pH of the waste material is of importance to inhibition or activation of the polymerisation.

4.5   Mechanisms of degradation

Organic solidified waste materials generally are resistant against both physical and chemical degradation processes with the exception of oxidation. Oxidation is a consequence of the reaction of the polymer chains with oxygen. Because of this, the chains are disturbed. UV rays to a large extent stimulate this process. Frequently, fragility occurs. Erosion subsequently leads to fast disappearance of the oxidised layer. To a small extent, the solidified waste materials can be affected by the presence of water or other liquids. A slight swelling and leaching of soluble components is possible (Means, 1995). Solidified waste materials based on bitumen show a gradual diffusion of water in the asphalt. If hygroscopic salts are present, hydrates are formed, by which the osmotic pressure in the waste material increases. The solidified waste material is swelling and finally can drift apart. In general, solidified waste materials are hardly resistant against organic solvents like butadiene,

diethylether, dichloorbenzene and trichloroethane. The presence of acids and metallic salts on the other hand are causing few problems (Conner, 1990). To conclude, solidified waste materials are more or less resistant against bacteria and high temperatures. Certain S/S-waste materials based on organic binders are biologically degradable (Noyes, 1994), (POSW, 1990). Thermoplastics are more sensitive to heat than thermosets (POSW, 1990).

4.6 Methods of application

It is possible to create a building material fulfilling the leaching standards of the Dutch Building Material Decree, see paragraph 3.6. Usually the constructive quality of the solidified waste material is good. A high strength, between 15 and 100 MPa, and a low elasticity modulus (Drakin, 1992), (Holman, 1995), (Rebeiz, 1995) characterise solidified waste materials. Depending on the application this is positive or negative. Thermosets are more inflexible then thermoplastics. From the strength and favourable leaching of the solidified waste material one generally expects that it can be applied usefully and that it doesn't have to be dumped. Organic solidified waste materials can adopt various molds. Molded solidified waste materials on the basis of bitumen is mainly used in road constructions. Organic solidified waste materials can, as well, be used in more high-quality applications like roofing-tiles and sewers.

4.7 Expenses

The expenses/costs of organic solidified waste materials mainly are determined by the price and quantity of the additives. In general, less thermosets are necessary than thermoplastics whereas thermosets usually are lower-priced then thermoplastics (POSW, 1990). However, if waste materials of, for example, plastic bottles are used the expenses for the S/S-treatment with thermoplastics are much lower. In general, S/S-treatments on the basis of thermoplastics requires more energy due to the higher temperature. These energy requirements can also be applicable for S/S-treatments on the basis of thermosets in case prior dehydration of the waste material is desired. Labour and equipment with regard to S/S-treatment is specialised and therefore expensive. Due to these factors the expenses for S/S-treatments with organic binders are significant higher than for cement based S/S-treatments, in order of $150 to $200 per ton product. On the other hand, these products could successfully be applied due to the good constructive properties.

4.8 Environmental aspects

S/S-treatments based on organic binding agents can, on a number of points, provide a positive contribution to the state of the environment. First, leaching of heavy metals and organic contamination is strongly diminished. Second, the size of dumping ground would be decreased because of an efficient utilisation of most of the Stabilisation/Solidification-waste materials based on organic binders. Third, the products could prevent usage of primary raw materials. Fourth, it is, by S/S-treatments on the basis of thermoplastics, possible to use waste materials as binding agents, a waste-to-waste approach. To conclude, volume reduction can occur as the polymers have a higher density as the monomer (Colombo, 1988).

Adverse consequences for the environment are the emission of components during the Stabilisation/Solidification process itself and the usage of energy. After the polymerisation, water

can stand still on the surface of the solid substance. This water has to be drained away and possibly has to be purified (Conner, 1990). By means of increased temperature by usage of thermoplastics, volatile components can disappear (POSW, 1990). These have to be caught. Along with the usage of thermosets, extremely harmful gasses can be released (POSW, 1990). Energy requirement of the process does arise out of increasing of the temperature necessary for the melting of the polymers and the drying of the waste material. Temperatures between room temperature and 350^0C are required.

5.   Thermal S/S-treatment

In the Netherlands, experience has been gained since 1989 with sintering of soil and polluted harbour dredging sludge. This has resulted in gravel that till now is not commercial. In Japan, the melting / vitrifying of purification silt is operational. In principle the concept originated from the oxidising melting. These days, the deoxidising melting of complex waste materials is particularly investigated, producing a crystalline material.

Thermal S/S-treatment is different from the S/S-treatments discussed above in that no binders are added. The S/S-treatment is based on the re-arrangement of molecules, atoms and ions at elevated temperature. There are three different techniques: vitrification after melting the waste material, crystallisation after melting the waste material and sintering, but first attention is paid to the pre-treatment required.

Before waste materials can be sintered or melted a number of pre-treatments are necessary. Supposing that the waste material contains sand and coarse parts these can be removed in order to concentrate the waste material. After that waste materials can be dehydrated, in the case that the dry substance proportion is lower then 50%, and afterwards can be thermally dried or dried by pyrolysis as far as the dry substance proportion is 85%. For crystallisation of waste materials the composition of the basalt is relevant. In order to create a good composition additives, mostly waste material, are added. Paper waste, industrial waste materials or fly ashes can provide the required calcium oxides, asbestos the required magnesium oxides and mineral silt the required silicon oxides. Remnants of batteries also can be added. During glazing of waste materials adding of sodium, boron or aluminium oxides can be necessary. For thermal S/S-treatment of fly ashes an extra pre-treatment is required. Due to the surface tension the ash stays on top of the fusion. The pre-treatment includes the application of a pressure.

The pre-treated material is placed into an oven and heated up to the desired temperature. For melting the temperature is between 1400°C and 1500°C. A vitrified or crystalline material is obtained depended on the follow-up treatment. Properties of the vitrified and crystallised product are furthermore determined by the melting conditions, reducing or oxidising. Typical sintering temperatures are between 800°C and 1150°C.

After melting, the material is cooled. Rapid cooling results in a vitrified material. A possibility is to plunge the fusion in a tray of cold water by which granulates and steam is created. Sprinkling of the material also is a possibility. Mainly supervised cooling down is used by which a crystalline

material is created. A solidification time of approximately 3 hours at a temperature between 800°C and 1400°C is required. The temperature depends on the waste material mixture. At higher temperatures several metals are making up crystalline materials in the form of oxygen. In that case crystallisation takes less time as crystallised seeds are growing.

In addition to the cooling, the follow-up treatment consists of the processing of the flows of the remnants. During the drying period of the waste, flue gas with organic components and water vapour is created. In case of deoxidising melting metal concentrates, mainly zinc and lead, are arising. These components can be recycled or have to be dumped.

5.1   Leaching

Under deoxidising circumstances, some components are not admitted in the product. Components with low boiling point, like cadmium and lead, are evaporating. Sensitivity of silicon, aluminium and calcium for leaching is determined by the admission in the 'lattice'. If an component does not fit into the 'lattice', like for example copper, it will be pushed out during the glazing, which starts out of the middle. The glassy product therefore shows an increased concentration of components, easy to erode, on the surface. Leaching of copper and zinc for example can meet the requirements set in the Dutch Building Material Decree but is quite pH dependent (Van der Sloot, 1996). In presence of oxygen, the relatively immobile chromium (III) is oxidised into the more mobile chromium (VI). Some of the sulphates are dissociated at a temperature above 800°C, at deoxidising as well as under oxidising conditions. The remaining sulphates are leaching easily under deoxidising conditions. Scrap of chlorides is dependent on the conditions. Under deoxidising conditions the concentration remains the same but through adding oxygen the concentration can decrease with 30%. High concentrates of salts, chlorides, fluorides and sulphates can interfere with the process of glazing and therefore request addition of extra additive (Noyes, 1994). Although the leaching behaviour of crystalline materials is better than that of glassy materials, leaching of vanadium, copper, antimony and arsenic remains a problem. Even though the ceramic material contains pores, the components are bound stronger in the structure then in the melt/crystalline material.

5.2   Properties of waste materials

Research has been performed on sintering of polluted soil and dredging sludge. The polluted soil and dredging sludge contain sufficient clay-like material in order to give a ceramic product. The melt/crystallizing process is implemented on hazardous waste materials with mineral and organic contamination like residue from soil sanitation, cleaning of screen sand, polluted soil and dredging sludge and sewage silt. As additives, fly ashes of industrial waste materials, asbestos and batteries are mentioned. An example is the melting of 60% polluted soil and dredging sludge with 40% fly ash/sewage silts considering that the polluted soil and dredging sludge contains to little calcium- and magnesium oxide. Vitrifying techniques have been applied among others on sewage silt. The desired properties of waste materials particularly consist of the percentage of the mentioned oxides of the basalt composition. Too many salts can create corrosion. Otherwise no requirements have to be met with reference to the chemical properties of waste materials. Organic contamination like dioxins are completely dissociated during the melting. Energy getting released could possibly be used for the melting. Volatile components are ending up in flue gas. By oxidising melting, heavy

metals are completely admitted in the product. Certain heavy metals are desired because of the increase of the crystallization process. The dry substance percentage is brought, via pre-treatment, up to more then 85%. Waste materials already reaching this percentage therefore have the preference. If the waste material already is concentrated removal of coarse components is not necessary too.

5.3   Degradation mechanisms

Crystalline materials are thermodynamically more stable than glassy materials. The glazing technique is delivering a product sensitive to humus acids and frost/thaw cycles. Another disadvantage of the glassy material is that it behaves like a fluid. After quite a while the glass will sink. The most upper layer of the crystalline materials is sensitive to degradation mechanisms like erosion and wet/dry cycles. Otherwise the materials nearly are resistant.

5.4   Methods of application

Ceramic gravel has lower density than normal gravel. Through this, the density of concrete is lower and such as a higher construction is possible. The compressive strength of sintered waste materials is between 15 and 50 MPa (Nishigaki, 1997). Glassy materials are harder than the crystalline materials. The glass therefore can only be implemented in applications of low value. Applications include founding materials for roads, grit blaster and facing-bricks in garden (Van der Sloot, 1996). The constructive value of crystalline material in general is better than that of glassy material. One therefore expects a high-grade application like for example the replacement of basalt blocks in dike construction. Moreover, the quality of crystalline material is as such that slabs for house building and tunnels can be produced. Because of the decrease in leaching most of the ceramic, glassy and crystalline materials can be used as building material.

5.5   Expenses

The expenses for processing are quite high. Part of the costs is determined by the high demand of energy. Generating energy out of flammable waste materials can significantly reduce the costs. The remaining expenses are in the purification of flue gas and the blending of waste material and additives. Due to the usage of hazardous waste materials the conditions of employment are expensive. For glassy and crystalline materials the costs are between $75 per ton product and $350 per ton product. The large variation depends on whether or not it is possible to regain energy out of the waste material. The expenses for ceramic products are approximately $125 per ton product. On basalt blocks a small profit could possibly be earned, as till now they are imported. At the moment, digging-up of gravel is inexpensive; due to the broadening of rivers a large quantity of gravel is released whereas the product is sold for $7.50 per ton. One can not expect that the sale of gravel will earn money. The sale of solidified waste materials as tiles also will not be high as the market is quite small. Profit of high quality slabs in the building industry is estimated at $100 to $200 per ton product. Anyhow money has to be contributed in order to sell the product despite of the saving of dumping expenses.

5.6 *Environmental aspects*

The negative contribution of the technique to the environmental problem mainly is the consumption of energy. This is determined by pre-treatment as well as by melt- or sintering-temperature. For sintering techniques the energy consumption is less than for melting. Moreover there is a small difference in energy consumption between glazing and crystallization. A second negative contribution is the release of flue gas and possibly other pouring of the waste material during deoxidising melting. In the first place the reduction of volume is a positive contribution to the environment. By drying the waste material, burning of organic materials and condensation of the waste material, the volume of the product is a factor 4 smaller than the untreated waste material. On the second place a product can be made, by melting and sintering of the waste material, which does not need to be dumped but could be utilized usefully. This provides a positive contribution onto the scarce supply of raw materials. Furthermore, usually no primary materials are used as additives. On the third place thermal S/S-treatment of waste materials is contributing to a decrease of leaching of hazardous components. The organic components are in general completely decomposed.

6. Conclusions

The three S/S-treatments discussed have different advantages and disadvantages, see table 1. First, S/S-treatment of inorganic waste materials based on the addition of cement is highly preferable for the replacement of low quality building materials. Because the material is sensitive to several degradation mechanisms, opposing the material to weathering conditions should be minimised. Besides that the end of the life of the S/S-waste material has to be taken care of.

Second, both S/S-treatment based on organic binders and thermal S/S-treatment is preferred for waste materials with a mixture of inorganic and organic components and for the production of high quality building materials. If a choice have to be made between the two, encapsulation mechanisms can be taken into account. The addition of organic binders leads to a product wherein the waste material is solely physical bound. On the contrary, thermal treatment destroys the organic components and lead to physically/chemically bounding of the inorganic components. Although this physical/chemical bounding of components in the thermal treated waste material, S/S-waste materials based on organic binders are less sensitive to degradation factors than thermal treated waste materials. The difference between the actual release of hazardous components of the two S/S-waste materials is not simply assessed.

In general, there is a lot of uncertainty about the actual quality of S/S-waste materials. Some adequate information and an assessment method is missing. More specific, an assessment tool for the long term release of components due to application conditions is desired. Therefore, more research is needed towards the long term behaviour of the different S/S-waste materials. Suitable empirical data beyond other more theoretical experiments can only be gained by the actual application of S/S-waste materials as building materials. While dumping capacity is more and more a problem, carefully controlled application of these materials in practice should be stimulated.

Table 1. comparison between Stabilisation/Solidification-treatments on the main aspects			
	Cement as a binder	**Organic binders**	**Thermal treatment**
Leaching	Organic components are hard to register Heavy metals can be chemically fixed Salts in general can not be chemically fixed	Physical encapsulation of most of the components	Organic components are decomposed Vanadium, Copper and Antimony hard to fix Other components chemically or physically fixed
Waste materials	Suitable for inorganic waste materials	Suitable for organic and inorganic waste materials	Suitable for organic and inorganic waste materials High amount of oxides preferable
Degradation mechanisms	Sensitive for erosion, wet/dry, frost/thaw, temperature changes, carbonation can have a positive effect	Oxidation, to a lesser extent the presence of liquids, high temperatures and bacteria	Sensitive to humus acid, crumbling and frost/thaw cycles
Application possibilities	replacement of gravel, embankment or foundation material, in most cases useful application is not allowed, because of the DBMD	High quality applications	Basalt blocks in dike constructions
Expenses	Approximately between $50 and $175 per ton product	Approximately between $150 and $200 per ton product	Approximately between $75 and $350 per ton product
Positive environmental aspects	Sometimes replacement of a building material	Replacement of a building material Waste-to-waste approach	Replacement of a building material
Environmental aspects	Additives	Additives release of volatile components	Energy consumption

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