INDUSTRIAL DEMONSTRATION PLANT FOR GRANULATION OF SIMULATED RADIOACTIVE AND TOXIC WASTES

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ABSTRACT

The paper describes an industrial demonstration plant which has been developed for the granulation of liquid wastes as well as sludges and dry fly ashes from the nuclear and non-nuclear industry. The plant is designed for a daily throughput of 15 t inactive granules, which are generated in a ploughshare mixer, using cement and bentonite or kaolin as matrix material. The green granules have to spend two days at elevated temperature and humidity in a series of hydration units.

INTRODUCTION

At the WM'82 Symposium, the basic concept of the in-situ solidification technique for the disposal of LLW and MLW was already presented.[1] In contrast to established waste management concepts, the in-situ technique applies a containerless technique using preconditioned waste grout, which is fed through a vertical pipeline from ground level directly into an underground cavern.[2]

A main feature of this concept is the granulation of the liquid radioactive waste in a cement/bentonite matrix. The granulation technique is based on the experience of more than 100 tons of granules produced in a pilot plant of F. J. Gattys Company.[3]

Recent R&D efforts arrived in planning and construction of an inactive industrial granulation plant with a capacity of about 3000 t/y (3 shifts per day operation).

This plant-now in full production-is described in detail in this paper. The concept of the plant was to enable granulation and coating of radioactive liquid wastes as well as sludges, fly ashes and dried salts. Cement/bentonite or kaolin mixtures are used as matrix material. The granulation technique can also be applied for non-radioactive toxic wastes, e.g., fly ash, sludges from clarification, salt solutions, which are to be disposed of by means of the in-situ concept.

SYSTEM SELECTION FOR THE GRANULATION PROCESS

Two different mechanical systems which are appropriate for the granulation process, i.e., rotating dish as investigated by R. Koster and coworkers[4] and the ploughshare mixer as used by F. J. Gattys Company[3] have been compared in the first phase of our R&D program. In contrast to the rotating dish, the ploughshare mixer represents a closed system, which can be well adapted to treat radioactive or toxic liquid wastes. Furthermore, the fabrication of specified polydispersive granules with a significantly higher density (2.5 - 2.7 g/cm^3) and smaller porosity, favored the application of the ploughshare mixer as granule generator rather than the rotating dish. Finally, the higher mechanical strength and the better leaching resistance of the granules produced in a ploughshare mixer have influenced the choice.

DESCRIPTION OF THE DEMONSTRATION PLANT

The design capacity of the inactive demonstration plant was based on the liquid MLW and LLW concentrates arising from the projected German reprocessing plant, which amounts to roughly 2 m^3/d. The experienced relationship:

$$\text{mass of granules/liquid waste volume} = 7.2\text{-}7.65\ t/m^3$$

amounts to a design capacity of the granulation plant of 15 t granules per day to be fabricated in a 3 shift operation, i.e., 5 t granules per shift. Figures 1 and 2 show the flow diagram and the general view of the demonstration granulation plant respectively. The total equipment covers silos for cement, bentonite, kaolin and dry wastes (now nitrates as waste simulation), three smaller silos for additive components, two storage tanks for liquid wastes, weighing and dosage equipment for solid and liquid materials, ploughshare mixer, a slow-moving heated conveyer belt as the hydration unit of discharged "green" granules, sieving device for removing over and undersized grain, a second very slow moving conveyer belt for the final hydration of granules, pneumatic system for the granules to the storage vessel of the product container filling station (presently baged in 2 m^3 big bags). Before bagging the hydrated granules will be sieved once more. Analog to process the main plant components are described below.

Feed System

The Feed System encloses two storage silos for cement, one silo for bentonite (30 m^3 each), one silo for salt or other dry powdered wastes (20 m^3) and three small silos for additives (0.5 m^3 each). All the silos are fitted with pneumatic charging and discharging elements. Pneumatic conveyers feed the weighing for dosage of solid materials and for the ploughshare mixer. The feed system for liquid waste covers two heated storage tanks (2 m^3) fitting with dosing equipment, which serve as feed adjustment units.

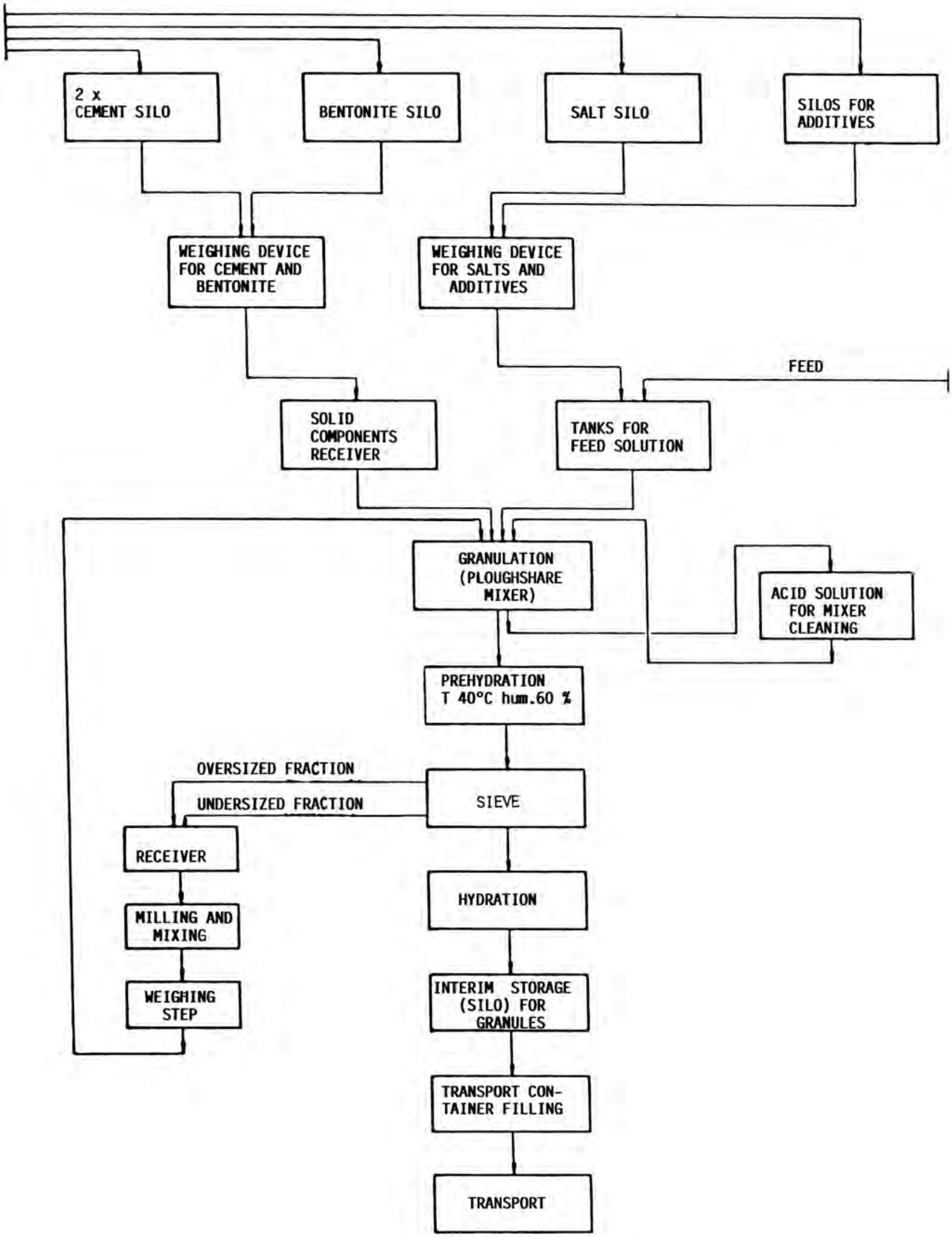

Fig. 1. Flow Diagram of the Facility.

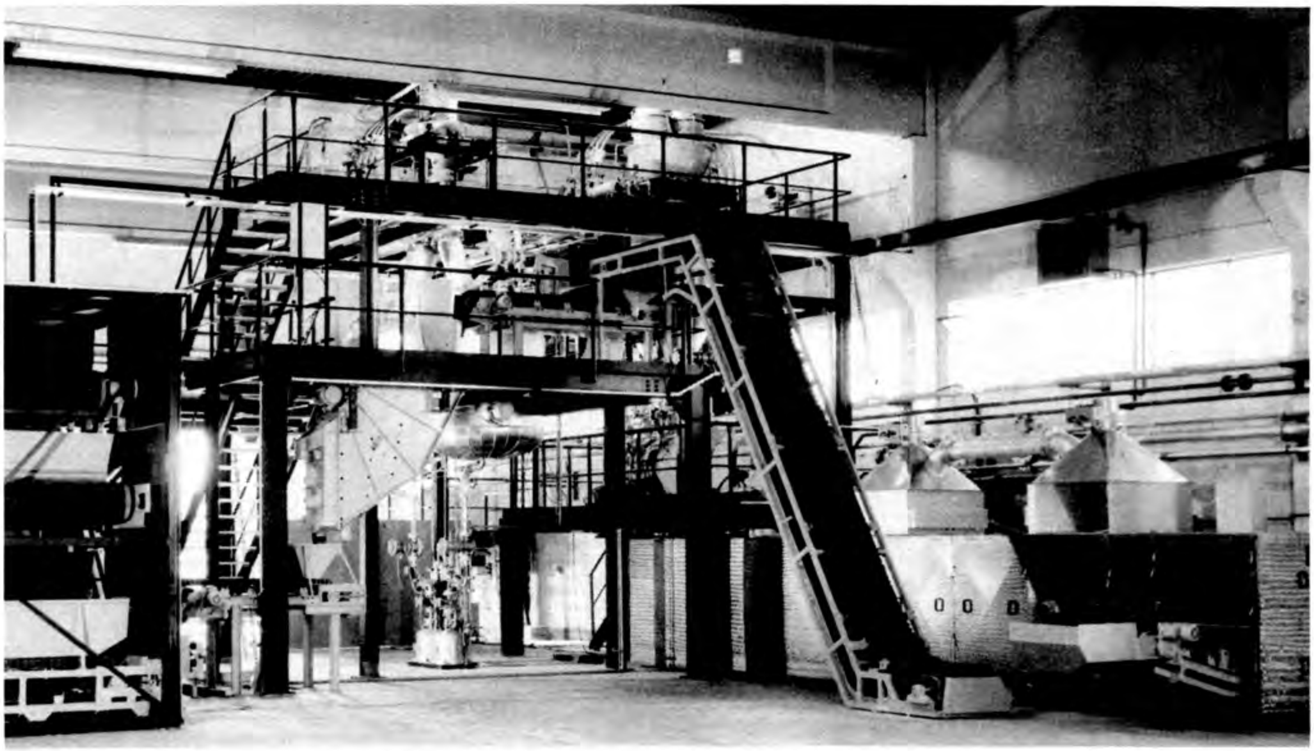

Fig. 2. General View of the Demonstration Plant

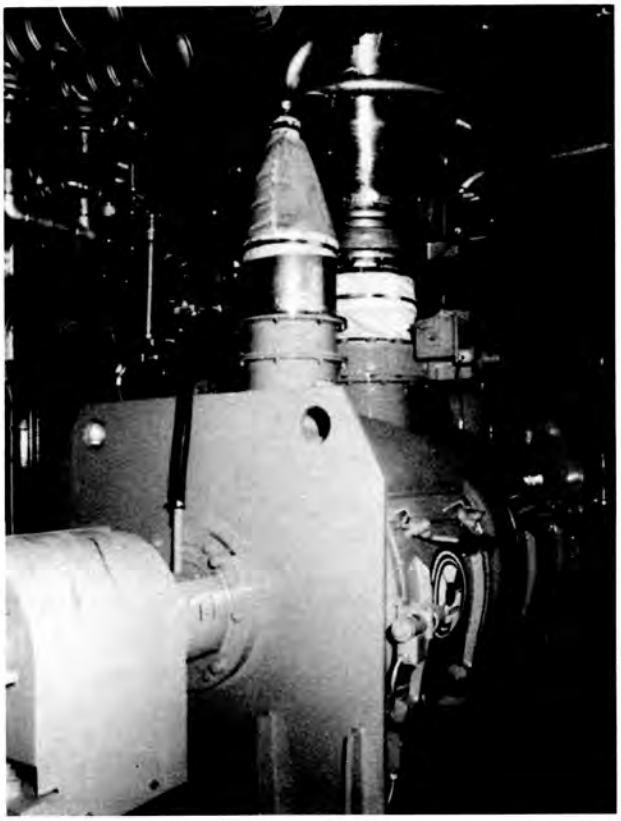

Fig. 3. Ploughshare Mixer in Operation

Fig. 4. Ploughshare Mixer with Open Sidedoor

Granules Generator

The granules generator is represented by a batchwise operating ploughshare mixer. Figure 3 shows the unit under operation with the feed dosing devices on the top, whereas Fig. 4 gives an insight into the unit through the intervention door with one batchinventory of green granules.

The capacity of the mixer is 1 m^3 and the degree of filling amounts to 35 to 45 Vol. %, which means a production rate of granules between 0.55 and 0.71 ton per charge. The granulation process itself represents a sequence of different operational steps as follows:

- charging the mixer with dry components of granules (cement, bentonite, dry waste)
- injection of liquid waste concentrates or water in case of granulation dry wastes
- agitation by permanent rotation of ploughshares in combination with a rotating cutter, which keeps the grainsize below 5 mm.

The duration of the whole granulation process as described above amounts to 45 minutes and is controlling the capacity of the whole plant.

The ploughshare mixer should be operated at a temperature of 35 ± 5°C. A higher temperature leads to a premature hardening of the mixture without production of granules, whereas a lower temperature favors the formation of granules bigger than specified. Another important process parameter for granulation in the case of cement/bentonite matrix is the water/cement ratio which was experienced to be 0.15. A lower ratio leads to prematured hardening of the mix without proper formation of granules whereas a water/cement ratio greater than 0.2 decreases the stability of the "green" granules as far as to disintegration to a grout.

Hydration Units

The complete hydration (hardening) of granules till they have enough stability for further handling requires about 7 days at room temperature. This time can be reduced by storing at an elevated temperature and air humidity. The operating time takes 30-60 minutes applied at a relatively thin layer of granules. After this operation, the "green" granules are ready for a first sieving step. The second hydration unit provides final hardening of the granules before interim storage and transport. The capacity of this step is large enough for a two-day production. Here the mean residence time of the granules is about 24 hours. This unit can also be operated at elevated temperature and humidity.

Sieving Units

Meeting the granule specifications is very important for the fabrication of the reference waste form, i.e., the granules/grout mixture, which is to be transported through a relatively thin pipeling (i.e., 50 mm) in the underground cavern as described[2]. The tolerance of the granule spectrum is within 0.3 mm and 5.0 mm with a maximum at 1.85 mm. The over- and undersized grain fractions of production charge (about 4.0 wt %) are separated by a sieving process step and pneumatically recycled via a mill to the ploughshare mixer, where they are added to a new production.

Cleaning of the Mixer

A special problem after a one day operation time is to clean the cement coated walls of the mixer. This cleaning is carried out by dissolving the coating with diluted nitric acid (0.1M ⟷ HNO_3). The resulting grout will be neutralized and also recycled to the mixer. The high degree of recycling as described above avoids any waste from the granulation process.

The Offgas System

The offgas from the total plant is cleaned by a special blow back filter system with high DF-values.

PRODUCT CHARACTERIZATION

The granulation process was primarily developed for the preconditioning of liquid LLW/MLW-wastes. The granule formula was subject to extensive R&D efforts resulting in several composition of different kinds of wastes.

The waste solutions with high contents of nitrates or phosphates (up to 500 g/l) contaminated with organic components have been granulated. The waste salt content in the granules amounts to 7 wt. % for liquid waste and can be increased up to 27 wt. % either by further concentration of the waste solution up to sludge formation or by modification of the matrix formula.

Figure 5 shows a random sample of a granulation batch spread on draft paper ruled in millimeter squares, which illustrates the grain spectrum of the polydispersive granules. Their main characteristics are given in Table I.

TABLE I

Main Characteristics of Granules with Liquid LLW/MLW-Waste

Composition:	75 wt. % cement 5 wt. % bentonite 20 wt. % waste concentrate
Product Density:	2,60 t/m^3
Bulk Density:	1,56 t/m^3
Open Pores:	15,0 Vol. %
Pore Size:	10^{-5} - 10^{-3} mm
Grain Spectrum:	0,3 - 5,0 mm
Impact Strength[4]	10^{-3} m^2 J^{-1}
Leach Rate in Dest. Water	$1,1.10^{-4}$ g cm^{-2} d^{-1}

Another granule formula was investigated for α- active waste solutions from fuel fabrication, which lays claim for higher leach resistance and longterm stability than a cement matrix. This stable matrix consists mainly of kaolin, a mixture of Al_2O_3 and SiO_2. The green granules are burned at a temperature of 1300°C for three hours. Table II contains the main characteristics of the ceramic granules.

Granulation of Nonnuclear Toxic Wastes

Recent R&D efforts were spent for the conditioning of nonnuclear toxic wastes by means of granulation with the objective of disposing this waste form by in-situ solidification in underground caverns. Subject of granulation in the pilot plant were following wastes: liquid wastes (salt solutions, sludges) with contents of heavy metals or toxic elements (Cd, Pb, Zn, Hg) fly ashes from waste incineration plants or from other industrial burning facilities. The resulting granules have been characterized and as example typical fly ash granules are described in Table III.

TABLE II

Main Characteristics of Ceramic Granules for α -Wastes

Kaolin	wt. %	56,7
Bentonite	wt. %	19,2
Al_2O_3	wt. %	3,7
$Si\ O_2$	wt. %	3,7
Waste Solution	wt. %	16,7
Product Density t/m^3		2,06/2,64$^{x)}$
Bulk Density t/m^3		1,30$^{x)}$
Open Pores Vol. %		4,9/8,2$^{x)}$
Impact Strength $m^2\ J^{-1}$		$3{,}0 \cdot 10^{-3}$

x) After burning at 1300 °C

TABLE III

Main Characteristics of Typical Fly Ash Granules

		Cement Matrix	Kaolin Matrix
Kaolin	wt. %	-	45,4
Cement	wt. %	47,0	-
Bentonite	wt. %	4,0	19,3
Ash	wt. %	32,0	11,7
Al_2O_3	wt. %	-	3,8
$Si\ O_2$	wt. %	-	3,8
Water	wt. %	17,0	16,0
W/C	wt. %	0,36	-
W/(C + A)$^{1)}$		0,21	-
Product Density t/m^3		2,43	2,49/2,04$^{2)}$
Bulk Density t/m^3		1,36	1,80/1.32$^{2)}$
Open Pores Vol. %		14,4	11,6
Impact Strength $m^2 J^{-1}$		-	$4{,}9 \cdot 10^{-4}$ 2)
Burning Loss %			18,3 % 2)

1) Water/(cement + ash)

2) After Burning at 1300 °C

CONCLUSIONS

The granulation technique has been developed to provide an interim waste form, which is to be disposed by in-situ solidification. A wide field of raw waste categories could be conditioned satisfactorily and the characteristics of the granules provide the conditions for a stable waste form in combination with the in-situ solidification concept. The R&D work done so far has proven the feasibility of the granulation process up to an industrial scale and the operational experience covers production of several hundreds of tons of granules using different categories of nuclear and nonnuclear toxic wastes.

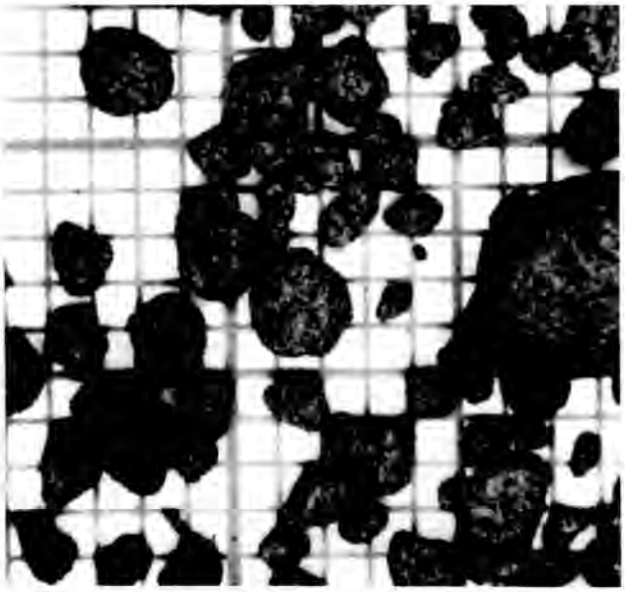

Fig. 5. Random Sample of a Granulation Batch.

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