

Treatment of Spent Resins and Sludges at the Mühleberg Nuclear Power Plant

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For conditioning spent resins and sludges arising at the Mühleberg Nuclear Power Plant, a solidification system has been installed in the existing radwaste processing building. The conditioning process includes the pretreatment of raw wastes, a thermal treatment of resins, and the immobilization in cement which has been optimized with regard to volume. Several recipes have been developed and qualified in accordance with the requirements to be met in Switzerland. Waste package types have been specified and subjected to a homologation. The system is being used for routine operation, basically without a problem. In connection with a process optimization program, the waste form can further be improved with regard to its water resistance. This is intended to be achieved by increasing the cement content, which can be made possible through additional ionic exhaustion of the cation exchangers. The production of 304 radwaste packages until now has shown that the intended resin or sludge loading of 300 and 200 kg, respectively, of dry waste matter per cubic meter of matrix volume can be reached.

1. Introduction

In light-water reactor plants, clean-up filters equipped with ion exchange resins are utilized for purifying water circuits and treating radioactive wastewater. Once exhausted their clean-up effect, the resins used in the filtering system are flushed into special collection tanks, where they remain until being processed as radwaste in batch operation.

For conditioning the spent resins to repository-suitable waste packages a new solidification system has recently been installed at the Mühleberg Nuclear Power Plant (KKM), which has been in operation since 1972. The resins, by means of this system, first are dewatered, dried, thermolytically broken down to some degree, and then solidified in waste packagings of 200 liters by using cement and additives. This system is also be suitable for the conditioning of the sludges accumulating in the KKM.

The waste packages to be produced from the raw wastes by means of the solidification system have to meet the requirements stipulated by the authorities as well as those concerning a future repository. An official permission is to be obtained to produce the packages. Regular matrix quality control is required during routine production. This is done by randomly choosing waste packages for taking samples from their contents or for later being subjected to non-destructive examinations.

An important requirement for the repository-suitable conditioning of radioactive waste is the optimum utilization of volume combined with meeting the specified waste package properties.

2. Characterization of the raw wastes

At KKM, a boiling-water reactor, both types of ion exchangers are utilized, powdered as well as bead resins, each one formed by a porous basic structure of polystyrene. Resin beads have a diameter of approximately 1 mm while powdered resin is characterized by an average grain size of about 40 μm . Both resin types are mixtures of strongly acid cation exchangers and strongly basic anion exchangers at mixing ratios between 1:1 and 3:1. The active centers of the cation exchanger consist of sulfonic acid groups while those of the anion exchanger consist of quaternary amino groups.

The sludges are residues from sedimentation tanks and sumps as well as from the laundry centrifuge. They basically consist of sand, dust and corrosion products or fibers and fluffs, respectively.

The average amount of wet resins to accumulate at the KKM is approximately 15 metric tons per year, having a specific activity between 10^8 and 10^{10} Bq/kg. Besides this, there are approximately 340 metric tons of non-conditioned resins in the interim storage facility resulting from operating cycles in the past. Compared to the above figures, the amounts of accumulating and existing sludges of 0.5 metric tons per year and 6.3 metric tons, respectively, are small. Their specific activity ranges from 10^8 to 10^9 Bq/kg.

3. Conditioning technique

The ABB technique called 'Cement Volume Reduction Solidification' (CVRS) has been chosen for realizing the project of a solidification system at the KKM, which allows to produce waste matrices containing dry matter of up to 300 kg of resins, mixtures of 270 kg of resins with 30 kg of sludge, or 200 kg of sludges, respectively, per cubic meter of matrix volume. The daily output amounts up to five waste packages. This system is able to transform not only the amount of resins and sludges accumulating during normal plant operation but also the raw wastes being temporarily kept in drums at the radwaste interim store into waste forms suitable for final storage.

The process principles are shown in the flow diagram presented by Fig. 1. It can be divided into the following subsystems:

Waste preparation

The resin-containing drums kept in the interim store are transported to the radwaste processing building where they are opened and tipped, using a special drum emptying station to do that. The resins are flushed out of the drums with demineralized water by means of high-pressure spray devices, and transferred to a resin sedimentation tank to be chosen in advance according to the type of resin being processed. For resins resulting from current operation of the KKM, the step described before is omitted. Separated according to their origin, those resins are collected in the resin sedimentation tanks and conditioned in batches.

With the help of remote-controlled devices, the sludge-containing drums are placed into a shielded drum-tipping device. There they are opened and emptied, and their contents are successively poured in small amounts onto a grating. After foreign materials have manually been eliminated above the grating, for further processing, the sludge reaches a reservoir which serves also to adjust certain parameters such as particle size, content of solids, and foaming characteristics.

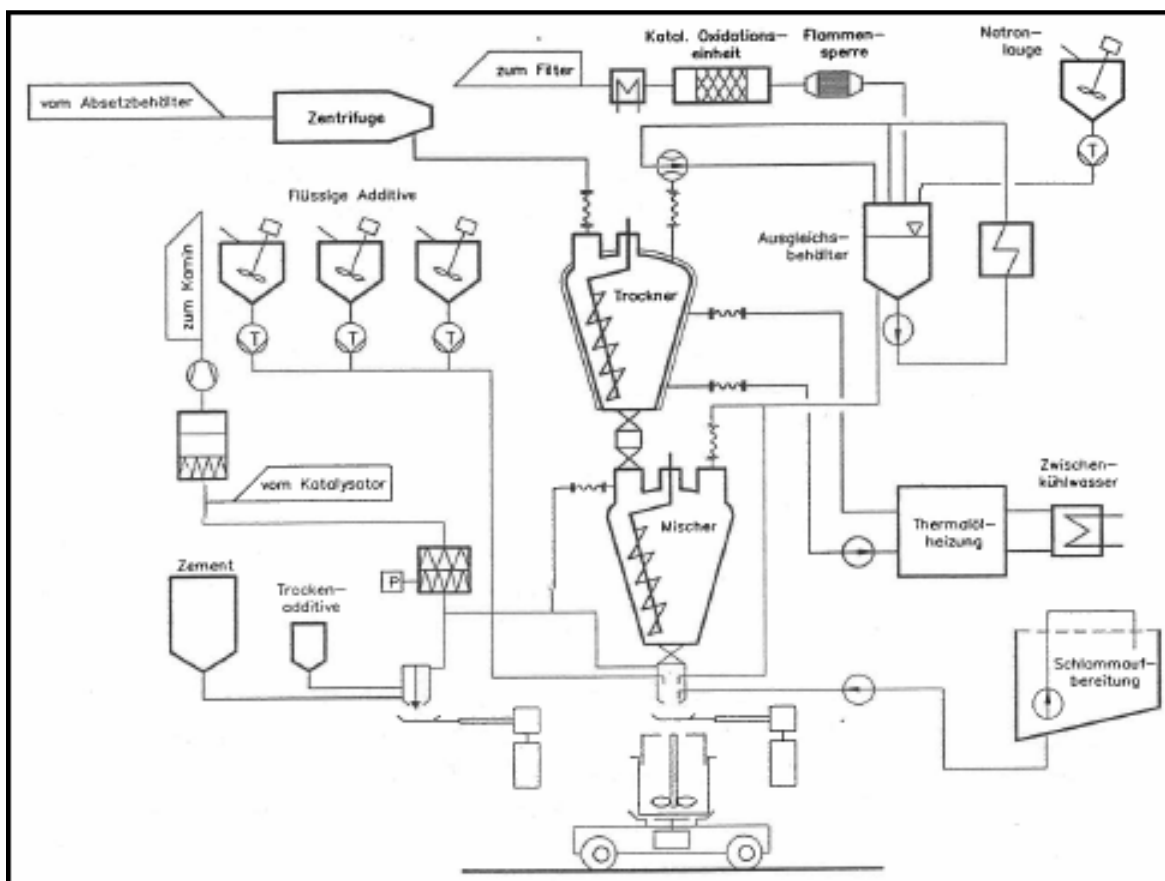


Fig. 1 Flow diagram of the CVRS solidification process

Thermal treatment of resins

The resin suspension in the sedimentation tanks are dewatered by means of a decanter centrifuge. For subsequent thermal treatment, the dewatered resins are conducted to a conical dryer, where they are first dried at a temperature of 100°C to remove their residual moisture, and then subjected to further treatment at a temperature of approximately 150°C which causes the structure of the resins to alter by splitting off organic decomposition products such as methanol and amines.

The water vapor that has been driven out and the released decomposition products accumulate in an auxiliary system. This system includes an equipment for destruction of the decomposition products, operating according to the catalytic oxidation principle. The condensate arising is temporarily stored and, in the subsequent cementation process, used as mixing water to be mingled for the most part with the resins in a downstream-arranged mixer.

The system components involved in the thermal resin treatment process contain nitrogen in order to produce an inert atmosphere.

Solidification

The pretreated resins or prepared sludges, respectively, are filled into standardized cylindrical stainless steel waste containers of 200 liters equipped with built-in stirrers and then solidified by mixing them with cement and additives. This process takes place in a remote-controlled filling station. A filling adapter facilitates the filling proc-

ess to be carried out under optimum volume utilization. Adapters and stirrers remain in the respective waste packages.

A transfer trolley is used for transporting the waste container to the different handling stations. The trolley is additionally equipped with an elevating device allowing the waste containers to be docked to the filling station as well as to the stirrer actuator at the solids dosing station.

Besides fully automated closing of the waste containers with so-called 'jet ring seals', remotely handled matrix samples are possible to be taken out of the drum and filled into sample tubes by means of a dosing device. In addition to this, wipe test samples can also remotely be taken from the surface of the waste containers.

Interim storage

The filled drums are transported to their storage positions in the radwaste interim store by using remote-controlled means of transport and hoisting equipment. They are stored there until being transported to a future repository.

As a result of thermal treatment, the resin load in the cement matrix can be increased by 50 % compared to conventional techniques. In addition to this, the matrix properties of solidified resins are positively influenced with regard to their suitability for the repository, e.g. compressive strength and leach rate as well as resistance to water and sulfates.

The CVRS solidification system has been installed in the existing radwaste processing building to replace one of two originally existing centrifuge lines. It consists of different components for dewatering, drying, thermal treatment, mixing dry matter with water, for dosing liquid and solid constituents directly into the waste container, as well as for homogenisation. The vertical arrangement of the components, one on top of the other, allows the resins destined for solidification to pass on from one process step to the next by gravity, as far as to the waste container.

4. Qualification of the waste forms

4.1 Requirements for the waste matrix properties and licensing

In Switzerland, the Swiss Federal Nuclear Safety Inspectorate (HSK), within its range of surveillance, is responsible for granting permission to the owners of nuclear plants to condition and temporarily store their radwaste. The respective requirements to be met have been stipulated in the HSK-Guideline R-14 'Conditioning and Interim Storage of Radioactive Waste'. They include binding principles with regard to waste package types and conditioning techniques as well as to waste matrix quality control, documentation, and quality assurance.

In order to be accepted at a future repository, the radwaste packages must additionally correspond to the requirements of the National Cooperative for the Disposal of Radioactive Waste (Nagra), i.e. their [acceptance regulation](#) and [preliminary acceptance criterias](#) must be obeyed as well as the corresponding [operational procedures](#).

According to 'HSK-Guideline R-14' and the repository requirements stipulated by Nagra, the waste form has to comply with the following properties:

- to have solid or solidified form
- to be stable and have structural integrity, at least until being disposed of at a repository

- to be hardly dispersible
- to be resistant to aqueous media
- to be hardly combustible
- to contain as little organic matter as possible
- not to have unnecessary hollow spaces

Plastics, bitumen and cement are regarded as solidification matrices.

After a curing time of 90 days, the cement matrix is required to have reached a compressive strength of not less than 10 MPa. The leaching rate for ^{60}Co as well as for ^{137}Cs , determined at specimens having passed the same time of curing and subsequently being exposed to both demineralized and gypsum-saturated water for 150 days, is required not to exceed the empirical value of 5 $\mu\text{m/d}$. In order to demonstrate form stability of the cement matrices for the intrusion-of-water case, the specimens are subjected to measurements concerning their water and sulfate resistance. This criterion is met when there is no qualitative difference in the appearance of form and surface structure of leached specimens compared to non-leached reference specimens, and when the compressive strength after leaching, also compared to that of reference specimens, has not decreased by more than 30 % and, at the same time, does not fall below the specified minimum. The measuring method is based on the experience of the Paul Scherrer Institute (PSI), where the matrix parameters usually are determined.

On the basis of specifications to be prepared by the waste producer, describing the conditioning technique applied and the waste package structure, Nagra certifies the suitability of the waste packages for the repository. When this has happened, the HSK first grants a provisional clearance to the conditioning technique, valid for producing a limited number of packages within the scope of a homologation. The aim of this homologation is to verify quality and required properties of the waste form and the specified normal operation of the conditioning system. When the homologation has successfully been concluded, the HSK grants the definite clearance to produce packages in conformance with the homologated waste package types.

4.2 Evaluation and qualification of recipes

Prior to construction of the CVRS solidification system, within the scope of a recipe qualification procedure, it had been demonstrated by laboratory and full scale tests that waste matrices with a powdered resin content of 300 kg per cubic meter, corresponding to dry matter, meet the totality of both authority and repository-related requirements. On the basis of the above recipe, as it can be seen in Table 1, others have been developed including mixtures of powdered resin with sludges or bead resin as well as pure bead

Table 1 Qualified recipes; waste loads expressed as dry matter in waste matrix

Waste type	recipe No	waste loading [kg/m ³]
Powdered resin	T11	300
Powdered resin / sump sludges	T12	275 / 25
Powdered resin / bead resin	T13	225 / 75
Bead resin	T14	280
Laundry sludges	T15	125 - 200

resin and pure sludges. This has been done with the aim to minimize the waste volume to be disposed of at a repository by maximizing the waste load of the individual package.

In Fig. 2, waste loads for different recipes are shown. As a whole, 74 different laboratory mixtures have been produced from which the most suitable ones, with regard to the CVRS solidification system, have been chosen. This refers to five recipes (see Table 1) for the solidification of pure powdered resin, mixtures of powdered resin with bead resin or sludges, pure bead resin and laundry sludges.

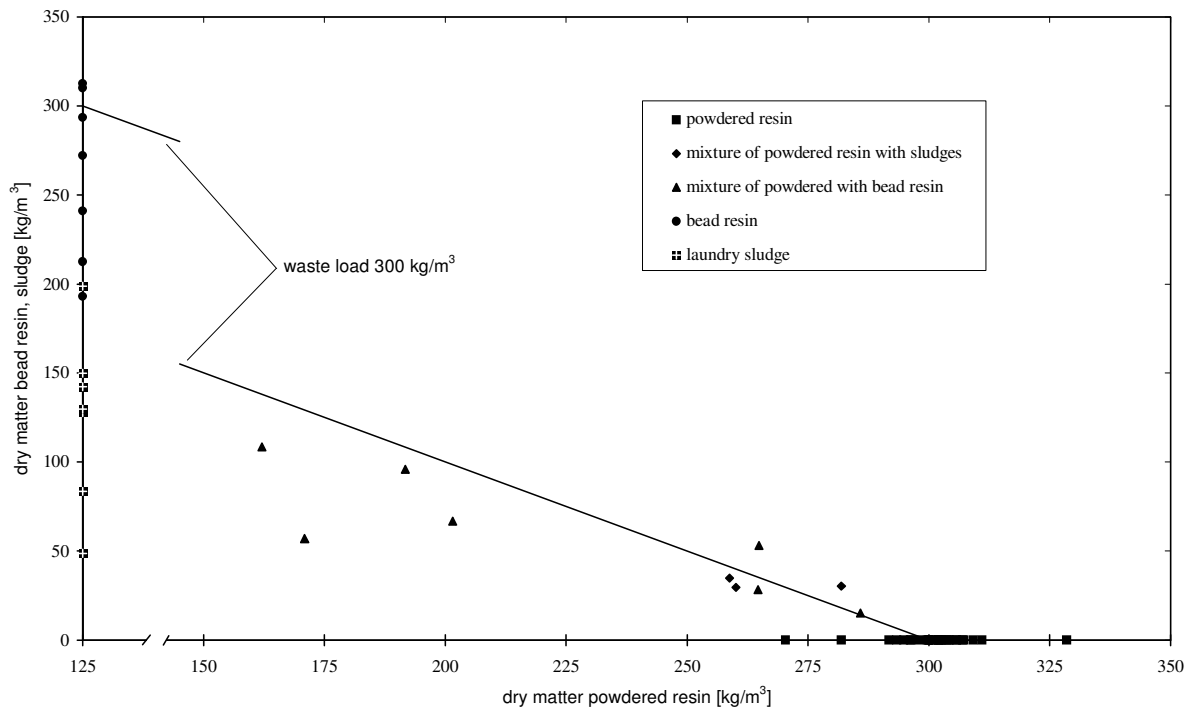


Fig. 2 Waste loads for different recipes which have been examined in laboratory scale tests. Besides the waste matrix requirements stated in Chapter 4.1, an aimed waste load of 300 kg/m³ of pure powdered resin and mixtures of it has been considered as an additional condition.

4.3 Homologation

Six waste package type specifications have been prepared for the conditioning of the waste types shown in Fig. 1. The suitability for the repository is certified and the provisional clearance is granted.

Within the scope of the homologation, proper quality of the waste form and specified normal operation of the CVRS solidification system have been demonstrated with test runs using inactive powdered and bead resin. For doing this, twenty packages of powdered resin and three packages of bead resin have been produced.

Proof of the waste form's quality is based on the results obtained from compressive strength measurements on matrix specimens after a curing time of 90 days, from non-destructive examinations carried out on the surface of cured waste matrices, i.e. visually evaluating the surface condition and checking the penetration behavior by means of a specified nail point, and from the assessment of the matrix's homogeneity on the basis of cut waste packages. As shown in Fig. 3, the entire utilizable volume of the drum has uniformly been filled out with homogeneously mixed waste matrix.

**Fig. 3**

Waste package of inactive powdered resin, cut open, produced in the CVRS solidification system. Section passing through stirrer shaft and axes of stirrer blades. Front showing drum opening without lid, including pressed-in adapter.

Subsequent to the inactive test phase and under realistic operating conditions, several packages of radioactive waste have been produced on the basis of each one of the five recipes. This refers to 63 packages of pure powdered resin, 4 packages of bead resin, 7 packages of powdered and bead resin mixtures, 5 packages of mixtures containing powdered resin and sump sludges and 5 packages of laundry sludge.

Non-destructive examinations on cured waste matrices as well as compressive strength measurements carried out on sampled specimens have demonstrated that sufficient strength and comparability to the results of recipe qualification is given. Exemplary in Fig. 4, the relation existing between compressive strength and matrix density is shown. The results of the measurements performed during recipe qualification as well as those of all 80 specimens sampled up to now have been taken into consideration for this. Correspondence between the results can clearly be seen, except for those concerning bead resin (Recipe No. T14). The effect of subjecting the cation exchangers to additional exhaustion with lime milk (see below) can be distinguished by the increasing density and compressive strength values for the specimens of recipe No. T11.

The other matrix parameters, which determination needs up to 240 days, are available in the scope of waste package quality control during production.

4.4 Waste package quality control

In order to prove that the waste matrix and thus the waste packages produced meet the required properties, quality assessments are made about them at random. For doing this, individual waste packages are chosen from regular production in order to take samples of their contents or for later being subjected to non-destructive examinations.

The matrix samples that have been taken are examined with respect to compressive strength, resistance to water and sulfates, as well as to leaching rates. Due to the specified measuring procedure, the period of time between sampling and availability of the results of examination amounts at least to 9 months.

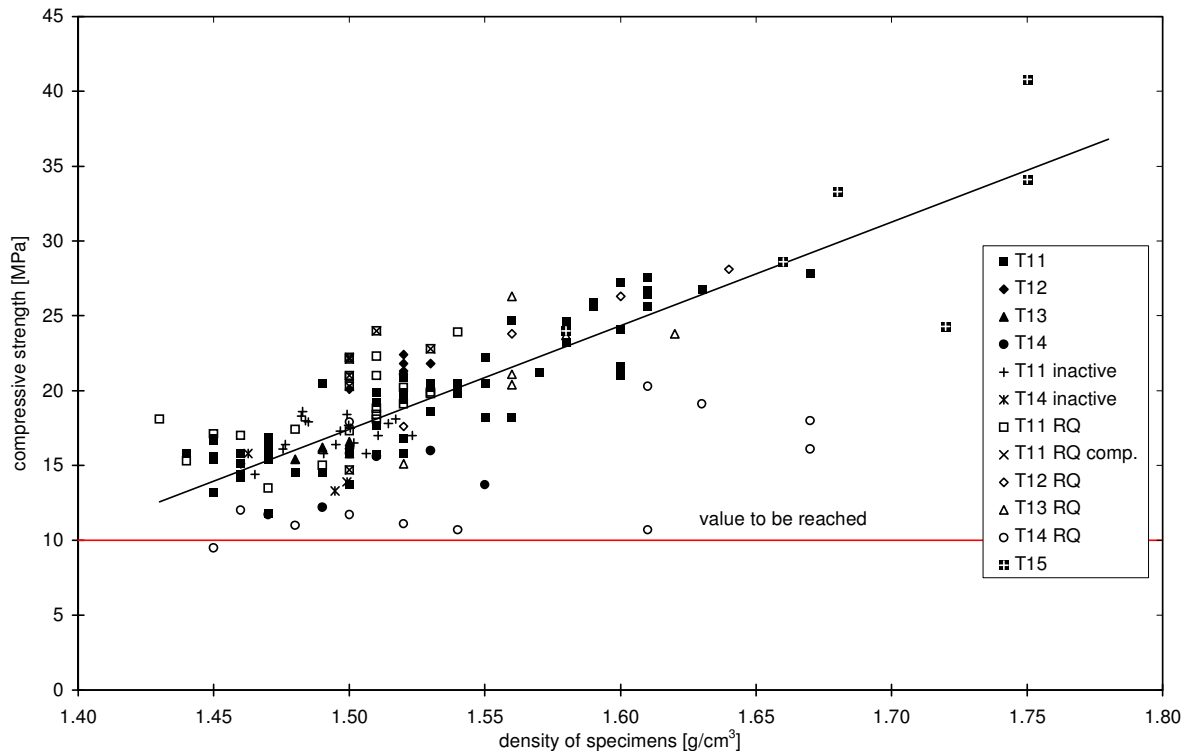


Fig. 4 Compressive strength of the specimens after a curing time of 90 days. Except for recipe No. T14 (bead resin), the results obtained during recipe qualification (RQ) correspond to the properties determined for the waste matrices produced in the CVRS solidification system. The RQ recipes which have a composition directly comparable to that of recipe No. T11 have been marked (comp.). The recipe qualification tests have not been taken into consideration for calculating the regression curve.

5. Operational experience gained with the CVRS solidification system

The CVRS solidification system has successfully been operated since the beginning of 1996. The conditioning of the waste packages, produced until now, took place in routine operation and basically without any problem.

During the homologation, an increasing level was observed in some packages due to swelling of the waste matrix after stirring had stopped. The consequence of this behavior is that the originally established maximum level has to be reduced. A reason for this could be that the volatile amines, which have formed during the thermal treatment, get bonded with the partly loaded cation exchangers and, in the subsequent solidification process, are released again due to the alkaline medium created by the addition of cement. This phenomenon of swelling has neither been observed during recipe qualification nor during the full-scale inactive tests. This could be explained by the fact that in both cases the resins had definitely been exhausted by 25 % of their capacity while parts of the resins resulting from operation have much less exhaustion.

This is the reason why, already during the homologation, for the production of 13 drums lime milk was added to increase the exhaustion of the cation exchangers. With this measure, it was possible to reduce the swelling effect. Excess lime, however, can cause scale deposit formation and a release of the activity bonded with the cation exchangers. Subsequent to the homologation, during the first half of 1996, 121 out of 158 packages containing powdered resin were produced by adding different amounts of lime milk in or-

der to verify the behavior of the resins as well as to determine which amount of lime milk is required and in which process phase it should be added. The amount of calcium used per waste package reached up to 4.5 kg, and the corresponding ionic exhaustion of the cation exchangers ranged between 5 % and 100 %.

As shown within the scope of waste package quality control, some specimens sampled from packages which had been produced during the homologation (particularly those containing pure powdered resin) did not meet the parameter for water resistance. In order to counteract the decrease in water resistance, corrective actions had to be taken. Efforts have been made to increase the matrix's density and reduce the water/cement ratio. As shown by the lime milk experiments, the matrix's density, and consequently compressive strength, can significantly be increased by providing for an additional ionic loading of the cation exchangers (compare Fig. 5). When considering the reduction of the water/cement ratio, it was found to be appropriate using an alternative to calcium for the ionic exhaustion of the cation exchangers, preferably also an alkaline earth element. It was expected that the use of barium would cause the resin volume to shrink to a greater degree and hence the waste matrix to further reduce its water demand.

Other 62 waste packages have been produced within the scope of a process enhancement program, in which the lime milk was partly substituted by baryta water. The effect of additionally exhausting the resin by means of calcium or barium ions on the water/cement ratio can be seen in Fig. 5. The volume effect, i.e. the increase in density with simultaneous decrease in the water/cement ratio caused by lime milk and even more by baryta water can clearly be made out.

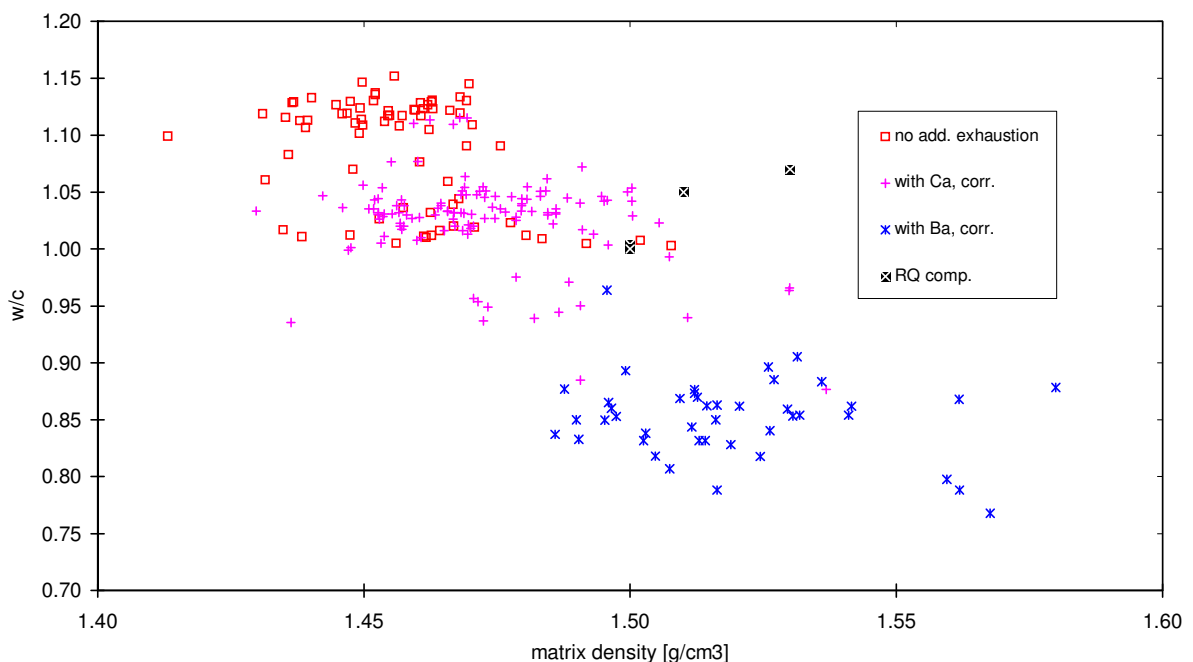


Fig. 5 Drums containing pure powdered resin, solidified according to recipe No. T11. The addition of lime milk and, to a greater degree, of baryta water causes the matrix's density to increase and the water/cement ratio w/c to decrease. In order to emphasize the pure volume effect, the masses of the calcium or barium ions, respectively, have not been taken into consideration in the calculation of density. To complete the picture, the comparable values resulting from recipe qualification (RQ) are shown.

First results obtained from these experiments have shown that, if calcium is substituted by barium, the resins become better exhausted, the curing process of the matrix does not suffer any delay as it has partly been observed in the case of calcium, and the addition of cement can be increased by 15 to 20 %. Matrix samples have been taken from 20 packages in order to determine their properties. However, final examination results of those samples, required for the definite clearance by the authority, are expected to be available not before the end of July 1997.

6. Present operational results

The CVRS solidification system is suitable for the conditioning of the resins and sludges either arising from current operation of the KKM or already being in existence by means of a technique which can routinely be applied. Pretreating the resins, the waste load of the cement matrix can be increased by approximately 50 % compared to conventional cementation techniques¹. In spite of cementation, resin conditioning with the CVRS system even results in a slight volume reduction of approximately 10 % since the wet waste, due to its lower bulk density, takes up more space than the waste matrix produced.

As shown in Fig. 6, a total of 304 waste packages have been produced up to now. As far as raw waste is concerned, a proportion of 241 of them contain pure powdered, 9 contain pure bead resin, and 42 of them contain pure laundry sludge. In 7 packages there is raw waste which consists of mixed powdered and bead resin while 5 drums contain a mixture of powdered resin and sump sludges. The average surface dose rate of the packages produced so far amounts to about 20 mSv/h for resins and approximately 0.5 mSv/h for sludges.

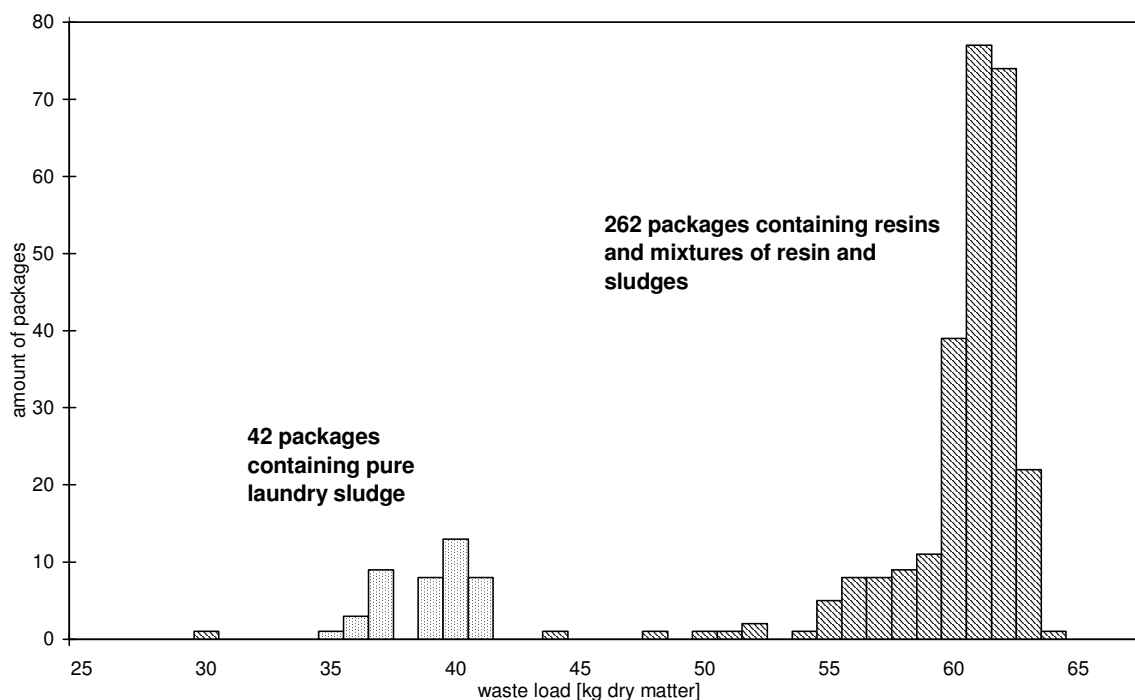


Fig. 6 Raw waste load of the waste packages produced up to now (i.e. end of 1996)

¹ Using an efficient technique without immobilizing the resins in a cement matrix, as for example the Hot High Pressure Method applied at the Nuclear Power Plant of Philippsburg, the resin load could be about doubled to around 120 kg dry matter converted to a package of 200 liters (see Trummer, L. et al.). However, techniques of that kind cannot be applied in Switzerland due to the requirements to be met by the waste matrix (see Chapter 4.1).

The experiences gained up to now show that an additional exhaustion of the cation exchangers is necessary in order to meet all the required matrix properties. The final results of the examinations carried out on matrix samples will be available in the course of 1997. However, it can already be stated that the addition of lime milk or baryta water influences the waste matrix in such a way that all required parameters are met.

Fig. 6 shows the waste load of the produced waste packages. In order to depict the plain waste load of the corresponding packages, the mass of the calcium or barium ions employed to exhaust the cation exchangers have not been taken into consideration.

The waste loads achieved for resins and sludges amount to an average of 283 kg and 183 kg, respectively, of dry waste matter per cubic meter of the volume to be disposed of, or in other terms, 299 kg and 193 kg, respectively, per cubic meter of matrix volume, matching well the aspired figures of 300 and 200 kg, respectively, per cubic meter of matrix volume.

7. Concluding remark

The method for determining the repository-relevant properties within the scope of a homologation as specified in the 'HSK-Guideline R-14' has shown to be feasible and, in principle, reliable. However, during the initial start-up phase of the CVRS solidification system it was observed that, as far as process adjustments are concerned which require authorizations, it is so time-consuming to determine the parameters important to the long-term safety of a repository that this can cause considerable delays in the specified normal operation. The aim should be to find timesaving examination methods for such cases.

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