ADVANCED CEMENT SOLIDIFICATION PROCESS

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ABSTRACT

The Advanced Cement Solidification Process, which features improved volume reductivity and properties of solidified wastes, has been developed to establish a better radioactive waste management system. Cement has been widely used as an inorganic solidification agent for the treatment of radioactive wastes generated at nuclear facilities. With current technology, borate waste solutions generated at PWR plant are neutralized with caustic soda and solidified directly with cement. This causes an increase in the volume of waste. Moreover, since borates retard the hydration of cement, the properties of solidified waste are not always such that meet the final disposal requirements. In order to eliminate these defects and to improve conventional cement solidification processes, SGN and JGC have conducted co-operative research, especially basic research on the pretreatment of borate. As a result of numerous experiments, a new process has been developed, by which solidified products with high volume reductivity and excellent physical properties can be produced. On the other hand, research and development work on a pilot plant have been carried out in co-operation with Kyushu Electric Power Co., Inc., including small scale hot tests of actual wastes at its Genkai Nuclear Power Station. A commercial-scale cold pilot plant was constructed and several proving tests have been conducted successfully.

INTRODUCTION

An increase in the amount of radioactive wastes generated at nuclear power plants along with an increase in their construction and operation, has created significant problems of radioactive waste management. Under such circumstances, the development of practical treatment processes for such wastes is an urgent task facing the world's nuclear power industry.

In order to store and transport medium- and low-level radioactive wastes generated at nuclear power plants easily and economically, it is essential not only to reduce their volume to the maximum extent but also to transform them into a solidified product so that it is suitable for final disposal and will maintain its chemical and physical soundness over a very long period of time.

For this purpose, the Advanced Cement Solidification Process with high volume reducibility has been developed. Cement has been most commonly used as an inorganic solidification agent for radioactive wastes at nuclear facilities, since it has many advantages as follows:

- It is standard, low cost embedding material.
- It is compatible with wet waste.
- Its hardened product is stable, and has high density and high mechanical resistance.

However, it has been generally observed that the volume of solidified products produced by conventional cement solidification processes becomes larger than the original volume of radioactive wastes. Moreover, the high quality solidified products are not always produced in cases where borate wastes generated at PWR plant are treated by such processes, because borates present in the wastes retard the hydration of cement and impede the progression of the hardening of cement paste.

In order to eliminate these defects of most of the conventional cement solidification processes, mainly related to borate wastes, SGN had been developing a new volume reduction and cement solidification system, in which a borate waste solution is pretreated and then overconcentrated. Independently of SGN, JGC was conducting basic research on the pretreatment of borates and on the hydration of cement.

In 1982, SGN and JGC agreed to begin co-operative work on the research and development of a volume-reducing cement solidification process, based on their past experience. After a series of basic experiments, particularly on the pretreatment of borates, SGN and JGC developed the Advanced Cement Solidification Process, by which the volume of wastes can be highly reduced and solidified products with good physical properties can be produced.

Small scale hot tests of actual wastes based on this process, with the co-operation of Kyushu Electric Power Co. Inc., were carried out at its Genkai Nuclear Power Station. In this hot test, the results of basic research were reconfirmed and the practicability of the process was proved. Based on preliminary performance test data on selected equipment, commercial-scale pilot plants were designed and constructed in both JGC and SGN laboratories, the former sponsored by Kyushu Electric Power Co., Inc., to carry out various demonstration tests on the operability, durability and optimal operating conditions of all equipment and systems. These tests have almost been completed, with the result showing that the process can be put into commercial service.

An outline of this process, mainly relating to treatment of borate waste, is described in this paper.

PROBLEMS WITH MOST OF THE CONVENTIONAL CEMENT SOLIDIFICATION PROCESSES

In most of the conventional cement solidification processes, the concentrated borate waste solutions generated at PWR plants are directly solidified with cement. This causes two main problems. These are:

- Borates ions present in the waste solution retard the hydration reaction of cement. This makes it difficult to obtain sufficiently hardened products with good physical properties.

- The volume of hardened products is larger than the original volume of wastes.

The first problem may be solved by the following mechanical or chemical means:

- Mechanical means
  When cement particles come in contact with a solution containing soluble borates, calcium borates is formed on their surfaces. It remarkably retards the hydration reaction of cement clinker mineral, such as calcium silicate, and also consequently setting time of cement. In order to make the hydration proceed, the calcium borate must be removed from the surfaces of the cement particles. This can be achieved, for example, by using a high-shear mixer.

- Chemical means
  Borates present in the waste solution can be transformed into almost hardly soluble borates. This eliminates the formation of calcium borates on the surfaces which retard the hydration and setting of cement.

In order to solve the second problem whereby the volume of solidified products must be further reduced, some means that would enable further concentrating of such solutions had to be developed.

SGN and JGC decided to solve these two problems by chemical methods and carried out extensive basic research on various pretreatment methods for borate waste solutions. SGN and JGC finally succeeded in overcoming the problems by developing an effective pretreatment method, by which insoluble borates are formed from such solutions.

BASIC RESEARCH

Basic Research on Pretreatment

An objective of the pretreatment is to transform soluble borates present in the waste solution into hardly soluble borates so that their retarding action on the hydration of cement can be eliminated.

Some alkali earth metal salts of boric acid such as calcium borate are known to be very insoluble in water. *For examples*, calcium borates exist in nature as born containing minerals. It is anticipated to be stable in the hardened cement matrix which also consists of calcium compounds. Therefore, in the basic research, SGN and JGC's efforts were directed toward finding methods by which insoluble calcium borates could be formed when a calcium compound is added to the borate waste solution.

In cases where the pH of concentrated borates waste solutions was on the acidic side, the rate at which calcium borates were formed was extremely slow, whatever calcium compounds were added.

When an alkaline calcium compound was added to an acidic waste solution, the reaction rate was extremely slow, so it seemed that no reaction was taking place. The alkaline calcium compound is solid. When its particles came in contact with a boric acid solution, a thin film of insoluble calcium borates was formed on their surfaces, and it prevented the particles from being dissolved in the solution and stopped their reaction.

In order to further advance the reaction, two methods were considered.

- To enlarge the lattice structure of the thin film of the insoluble salt so as to allow calcium ions to easily pass through the film.

- To promote the dissolution of the calcium compound under specific conditions.

It is well known that in cases where cement is mixed directly with a borate solution, the mixture does not harden neither develop strength even after curing for one month, but the addition of sodium hydroxide to the solution to transform boric acid into sodium tetraborate or sodium metaborate causes the mixture develop strength. This fact was effective in solving the problem.

Sodium hydroxide was added to a borate solution, and the solution was then mixed with a calcium compound. The mixture was continuously stirred. As the reaction advanced, a thixotropic paste was produced. The higher the concentration of boric acid, the more viscous it became. And it sometimes stiffened and remained in a nearly pasty condition only when the stirring was continued. When the stirring was stopped, it became a gel and was difficult to handle. By this pretreatment method, it was possible to obtain low soluble calcium borates but it was difficult to concentrate the solution.

In order to improve reaction conditions in the pretreatment step, such as reaction temperature, stirring conditions (stirrer type, blade shape, revolution speed), dosage of chemicals, method of dosage, etc., further detailed studies were conducted.

It was found that pretreatment under adequate stirring conditions prevented the formation of the pasty substance and produced precipitates of insoluble calciumborate. The precipitates are crystals having good sedimentation tendency and can exist stably in a cement matrix.

Basic Research on Mixing Ratio

The solid/water/cement mixing ratio to prepare a cement paste is determined according to the procedures shown in Fig. 1. The cement paste must have a sufficient consistency at which it can be poured into a container. The consistency or workability can be measured as flow values defined in JIS R 5201 or ASTM C124-71.

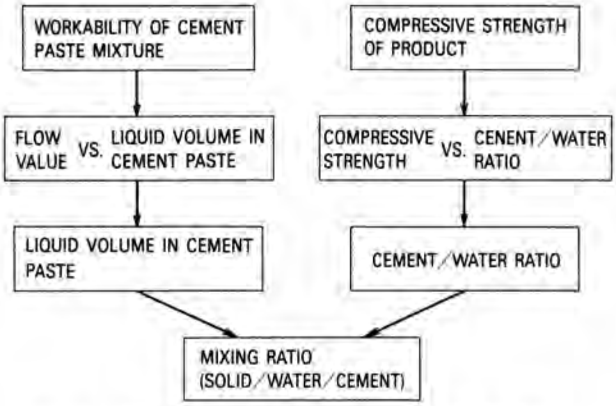

Fig. 1. Procedure of Design of Mixing Ratio.

Experiments showed that the consistency or workability of cement paste increased proportionally as the volume fraction of liquid in a mixture increased. The volume of liquid in a mixture can be determined if the target flow value is set.

Meanwhile, the strength of solidified products depends upon cement/water ratio in a mixture. The cement /water ratio can be determined if the target strength of solidified product is set. Since liquid volume determines the quantity of water, the mixing ratio can be determined if the consistency of a mixture and the strength of solidified products are set.

Experiments on consistency and strength showed that a mixing ratio of 50/30/20 (solid/cement/water) by weight was adequate in cases where the target flow value was set at 200 mm or larger, while the target one month compressive strength of solidified product was set at 20 MPa or larger.

HOT TEST

A series of small-scale hot tests of this process were carried out at the Genkai Nuclear Power Station of Kyushu Electric Power Co., Inc. The experimental results are summarized below.

- Calcium borate precipitates were successfully obtained in a pretreatment step.
- Pretreated waste solutions were concentrated. The concentrates were solidified with cement. Sufficiently hardened products were produced.
- In cases where the concentration of boric acid in the waste solutions was 12 wt %, the volume of solidified product became approximately 1/4 of that of their original waste solution.
- Solidified products showed good water resistance.

The hot tests confirmed the results of the basic research and proved that the process is effective in solidifying actual borate waste solutions.

BASIC PROCESS FLOW

The basic flow of the Advanced Cement Solidification Process is shown in Fig. 2. This process consists of the following three main steps.

Pretreatment Step

The pretreatment step, the key to the successful operation of the process, is indispensable for ensuring the hardening of cement to produce sufficiently solidified products, with good physical properties in a reproducible way.

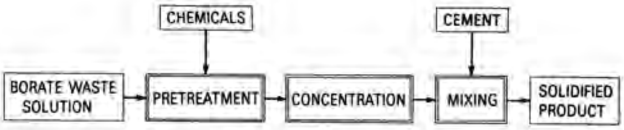

Fig. 2. Basic Flow Diagram of Advanced Cement Solidification Process.

In the pretreatment step, calcium borate is formed and precipitated. The precipitates are stable crystals and have good sedimentation properties.

Since dissolved borate, deterimental to the hydration of cement, can be converted into insoluble calcium borate precipitates, it has become possible to obtain sufficiently hardened products with good physical properties, which are suitable for waste storage, transportation and final disposal.

Concentration Step (Volume Reduction Step)

In this step, a borate waste solution is concentrated to such an extent that only a minimum quantity of water necessary for mixing with cement is left. This operation has become feasible by removing dissolved borate in the form of insoluble calcium borate showing good sedimentation.

From the viewpoint of reducing the volume of a borate waste solution, the most common method that enables the greatest volume reduction is to evaporate such solution to complete dryness. In the process, the borate waste solution is not evaporated to dryness but is concentrated to an optimum volume, because cement must be mixed with water so as to harden it.

The concentration step avoids technically difficult dry powder handling operations.

Mixing Step

An out-drum mixing method is employed in the mixing step. In order to produce solidified products having high strength and highly reduced volume, it is important to prepare a cement paste of good consistency with a minimum quantity of water. It is also important to increase the packing efficiency of such paste in a container. For these reasons, it is preferable to adopt the out-drum method, which can provide high mixing and filling.

Different kinds of cement can be used depending on requirements of the final product qualities. The results presented hereinafter are based on the ordinary portland cement (corresponding to ASTM Type I).

Advantages

The advantages of the Advanced Cement Solidification Process are:

- Based on 12 wt % of boric acid, the volume of solidified products produced by the process is 1/7 - 1/8 of that produced by conventional cement solidification processes.
- Solidified products having good physical properties are produced.

- The process is safe. The process does not need any flammable material. Moverover, it is a wet process, air-borne contamination due to radioactive nuclides resulting from a dry process can be avoided.

- All materials to be used in the process are readily available and inexpensive.

PILOT PLANT TEST FOR COMMERCIALIZATION

Examples of Typical System

As shown in Fig. 2, the process basically consists of three steps: pretreatment of borate waste solution, concentration of slurry, and cement mixing. With regard to the concentration methods and operating modes, several systems are feasible. Examples of a typical system are shown in Fig. 3.

System-1 is a continuous process and consists of three steps: pretreatment, overconcentration and mixing. The slurry, obtained in the pretreatment step, is evaporated and concentrated in the step of overconcentration. The concentrated slurry is cooled and mixed with cement. This system is of advantage in cases where there are frequent discharges of borate waste solution. Since the slurry is concentrated by evaporation, the concentrating vessel is equipped with a specially designed scraping mechanism so as to keep the heat transfer surface exposed at all times to the slurry. The mixer is also equipped with a similar mechanism. SGN has designed and built a pilot plant based on this system and has been conducting experiments.

System-2 is a batch wise process and consists of four steps. The concentration step in the basic process, which is shown in Fig. 2, is divided into two steps: solid-liquid separation and concentration of separated liquid. This system is advantageous in cases where discharges of borate waste solutions are less frequent. Calcium borate precipitates obtained in the pretreatment step have good sedimentation properties and easy to separate. This separated solid portion is sent to the mixer and the separated supernatant is concentrated by evaporation. Since borate precipitates can be almost removed in the separation step, a conventional type concentrator can be used.

With the co-operation of Kyushu Electric Power Co., Inc., JGC has built a commercial-scale pilot plant based on this system and has been carrying out various tests to put this System-2 process into commercial service.

System-3 is also a batch wise process, using pretreatment, concentration and cement mixing—depending on the basic data. These three steps can be operated in one or two stages. The system is based on the concentration under reduced pressure condition of the slurry, during and/or after the pretreatment step. The concentrated slurry is then mixed together with the binder. The concreted product is poured into a drum in the last step. This system has been developed with a view of reducing the number of equipment and making the entire system design compact. SGN intends to design a compact mobile unit based on this system, the corresponding tests are going on.

Pilot Plant Based on System-2

The effectiveness of system-2 process has been proven in pilot plant, which is outlined below.

Pretreatment:
A reaction vessel, equipped with a specially designed stirrer, was used. The stirrer served to effectively mix the borate waste solution with an added calcium compound. Crystalline precipitates of insoluble calcium borate were formed.

Solid-Liquid Separation:
A conventional type separator was used to separate the slurry into the supernatant and solid portions. The separated solids were sent to the mixer. The separated supernatant was first stored in a tank and then fed to an evaporator.

Concentration:
A small conventional type evaporator was used to concentrate the supernatant. Concentrated liquid was sent to the mixer and used as mixing water. Therefore, the supernatant was concentrated to the minimum

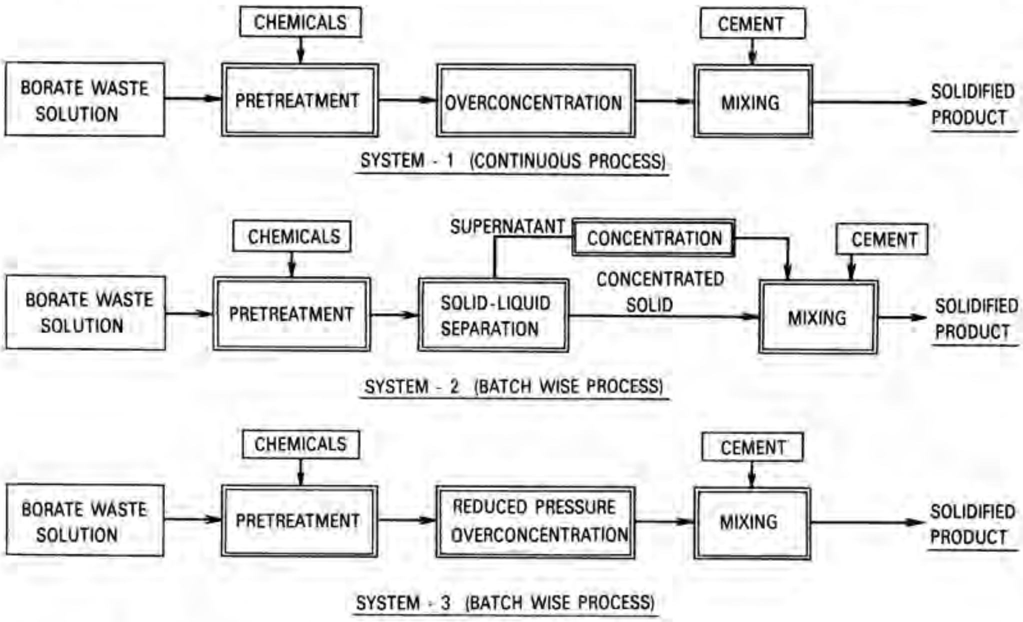

Fig. 3. Typical Flow Diagrams of Advanced Cement Solidification Process.

possible volume by which the separated solids could be mixed with cement.

Mixing:

The pilot mixer used has blades which rotate at high speeds. Weighed quantities of the separated solids and the further concentrated liquid were pre-mixed. The pre-mixture was well mixed with a weighed quantity of cement for a few minutes so as to obtain a workable cement paste. The paste was poured into a container. After curing the mixture at room temperature, a sufficiently and uniformly hardened product was obtained. After the mixing operation was completed, the mixer was easily washed.

A series of pilot plant tests on the performance, operation and durability of the equipment used in each step proved that the System-2 process successfully met all pre-set targets. Also, a large volume of engineering data including the operability and optimal operating conditions of the whole system was obtained. All experimental results showed that it would be feasible to put this process into commercial service. A conceptual design of an actual plant was carried out, using the experimental results. It was known from the conceptual design that a sufficiently economical and compact system could be constructed.

PHYSICAL PROPERTIES OF SOLIDIFIED PRODUCT

Several typical physical properties of solidified product obtained by this system-2 process are shown below.

Strength Development and Specific Gravity

The strength development of a solidified product obtained is plotted in Fig. 4. After it was cured for about one month, it showed a strength of more than 20 MPa. Even one year later, measurements showed that its strength was steadily increasing.

An electron microscopic observation of a cross-section of the solidified product proved that the calcium borate formed in the pretreatment step was also stable in cement matrix for a long period of time.

The specific gravity of the solidified product is about 1.8.

Water Resistance

The solidifed product does not lose its strength, as shown in Fig. 5, even if it is immersed in water for a long period of time. Its volumetric change was equal to or less than 1% in one year, with result that there was no appreciable change in its shape. It has good water resistance.

Leachability

The leaching rate of two typical nuclides, Co^{60} and Cs^{134}, measured by using a specimen, 45 mm in diameter and 44 mm in height, was as follows.

Co^{60} : 10^{-6} cm^3/cm^2. day or less

Cs^{134}: 10^{-4} cm^3/cm^2. day or less

The leaching rate of Cs^{134} can be further improved, if necessary, by adding zeolite or using blended cement.

Uniformity

A 200-liter (55-gallon) solidified product was produced. Samples were taken from the core to measure the specific gravity and strength. The measurements showed that the specific gravity and strength of the solidified product were uniform throughout product.

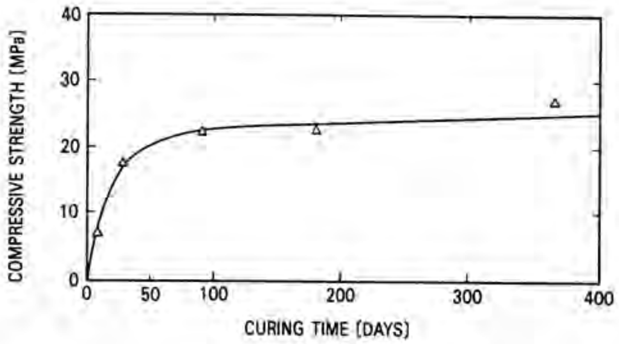

Fig. 4. Strength Development of Solidified Product Cured in Moist Air.

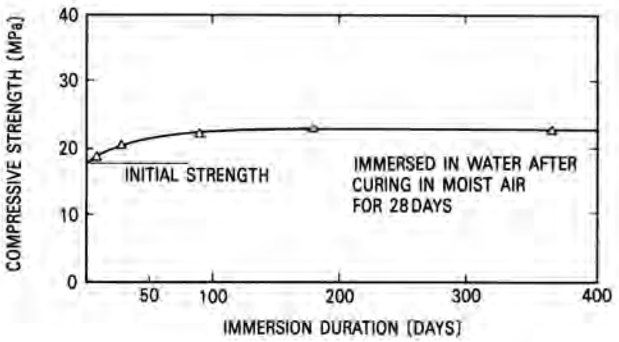

Fig. 5. An Example of Water Resistance of Solidified Product (Strength Development).

VOLUME REDUCIBILITY

The volume reducibility obtained by the Advanced Cement Solidification Process is shown in Fig. 6. When treating 1 m^3 of concentrated waste solution containing 12% boric acid, conventional cement solidification processes produce about 2 m^3 of solidified product, with the result that the original volume is increased. On the other hand, this process produces 0.25 m^3 of solidified product, resulting in the volume being 1/4 of the original volume. When compared with most of the conventional process, the volume of the solidified product obtained by this process is about 1/8. Thus, this process attains an extremely large volume reducibility.

Accordingly, this process is very effective in many respects, i.e., reductions in storage space, transportation costs, etc., when treating radioactive waste containing borates.

CONCLUSION

A method by which radioactive wastes containing borate generated at PWR power plants can be chemically treated in such a manner that insoluble borates can be formed has been established, and based on the method, the Advanced Cement Solidification Process has been developed.

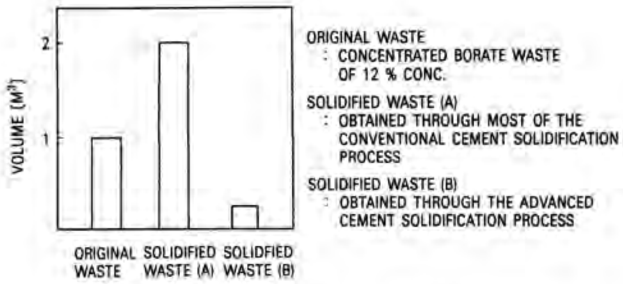

Fig. 6. Comparison of Volume Reduction.

- The volume of solidified products produced by the process is about 1/8 of that obtained by conventional cement solidification processes.

- The process produces solidified products having good physical properties. Such products are suitable for storage, transportation and disposal.

- Cement, used as a solidifying agent, is inexpensive.

- Radioactive wastes are processed in liquid or slurry form, so no airborne radioactive powders are produced. Thus, the process can be safely operated.

- The system is highly reliable and consists of practical equipment. Proving tests were successfully carried out on a commercial scale pilot plant.

- The pretreatment step of the process was proved to be practicable by numerous pilot plant tests and also by hot tests.