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Project Summary

Dewatering Wastewater Treatment Sludge by Clathrate Freezing: A Bench-Scale Feasibility Study

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Preliminary investigations were conducted on the technical feasibility of clathrate freezing applied to the dewatering of municipal wastewater sludge. This project has successfully demonstrated the fundamental feasibility of the process, although contact times of 15 to 20 minutes were necessary to achieve high dewatering. Also, other clathrating agents should be examined. Considerable work would still be required, therefore, for bringing the process to full-scale commercialization. The work was done under a cooperative agreement with the Metropolitan Sewer District of Greater Cincinnati, Ohio, subcontracting to Benmol Corporation, who initially suggested the process.

This Project Summary was prepared by EPA's Water Engineering Research Laboratory, Cincinnati, OH, to announce the major findings of a project that is documented in a separate report of the same title (see Project Report ordering information at back).

The Process

The clathrate dewatering process would use a liquid refrigerant to form a complex with the water in sludge. The complex, or clathrate as it is termed, freezes to form a solid crystal. In the clathrate crystal, molecules of water surround a molecule of clathrating agent. The water and clathrating agent are likely held together by a combination of intermolecular attractions and crystal geometry that permits the trapping of one molecule within the voids of another's crystal lattice. The clathrate freezes at temperatures above the freezing point of water. Therefore, if sludge is immersed in an excess of clathrating agent at a temperature between the freezing points of the clathrating agent and water, clathrate crystals could form without the formation of ice crystals. It is proposed that water inside sludge particles and cellular material will diffuse outward and form clathrate crystals in the bulk liquid phase, producing a suspension of totally dehydrated sludge particles, clathrate crystals, and the liquid clathrating agent. It should then be possible to separate the clathrate crystals from the sludge solids by virtue of their density difference, and thus effect a water removal and dewatering of the sludge. Upon melting of the clathrate, water can be separated and clathrating agent recycled to the process. Easily liquified compounds that form clathrates with water include propane, many Freons, other hydrocarbons and gases, and halogens.

Project Objectives and Methods

The objectives of this initial study were to concentrate on the three following concerns relating to technical feasibility:

(1) Extent of clathrate formation;
(2) Ease of achieving phase separations required for the process; and
(3) Extent to which water is removed from the bulk of the sludge solids.

In the preliminary study of technical feasibility, Freon-11 was used as the clathrating agent. Although liquid propane would be preferred for a commercial process due to its lower cost, working with Freon-11 was much easier. Propane studies would require higher pressures, and propane is flammable. With Freon-11 experiments can be conducted nearer to normal laboratory conditions with considerably less complicated techniques.

The feasibility was investigated in a simple apparatus where sludge and liquid Freon-11 were placed in a 1-liter test-tube shaped vessel, stirred with a laboratory mixer, and allowed to settle. The test-tube shaped vessel was immersed in a 1.5°C water bath. Primary, secondary, and mixed sludges were tested. The mixed sludge had a 60/40 volume ratio of primary-to-secondary sludge, typical of that processed at the Mill Creek Treatment Plant in Cincinnati.

Results

Average water removals by clathrating varied between 48 and 97.9 weight percent (9.25-52.6% dry solids in the product), depending upon contact time and sludge type. Sludge was mixed with liquid Freon-11 for both 10 minutes at a time and also for as much as 20 minutes with the phases separating but remaining in contact for as long as 2 hours. Single contacts and two-stage contacts (two repeated contacts of the sludge with pure Freon-11) were used. To obtain the higher degrees of dewatering, the longer and/or two-stage contacts were necessary. Clathrate crystals obtained were of two types, a rather soft grayish crystal with a molar ratio (water to Freon-11) of about 17 to 1 and a hard white crystal with a molar ratio of about 8 to 1. Procedures could be adjusted to obtain the latter kind of crystal which separated well under gravity. In summary, high water removals with good phase separations appeared to be possible.

Although basic technical feasibility was shown, considerable work would still be required to develop the process to the point of commercialization. First, the conditions favorable for high water removals need to be more accurately defined. Next, studies would be desirable with less expensive propane rather than Freon-11, and phase separation devices used in full-scale processes, such as hydroclones, should be evaluated. A careful economic analysis would also b desirable. Even though the process do show possibilities, it is fairly complex wi considerable development work still r quired. For the present, additional EF funding is not planned, but continu development by Benmol Corporation m take place.

The full report was submitted in fulfi ment of Cooperative Agreement No. C 810549 by the Metropolitan Sewer Distri of Greater Cincinnati, under the sponsc ship of the U.S. Environmental Protecti Agency.

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The complete report, entitled "Dewatering Wastewater Treatment Sludge by Clathrate Freezing: A Bench-Scale Feasibility Study," (Order No. PB 86-239 779/AS; Cost: $11.95, subject to change) will be available only from.
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