Wat. Res. Vol. 35, No. 14, pp. 3502–3507, 2001
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Printed in Great Britain
0043-1354/01/$ - see front matter

PII: S0043-1354(01)00048-3

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RESEARCH NOTE

HIGH-SPEED SLUDGE FREEZING

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(First received 28 April 2000; accepted in revised form 4 January 2001)

Abstract—The investigation examined the feasibility of applying a "high-speed" freezing technique, using liquid nitrogen freezing, to condition activated sludges and alum sludges. Experimental results indicate that the freezing speed is much faster than that adopted in most previous works on sludge freezing. Although the filterability and settleability of the alum sludge is improved by 3-min liquid nitrogen freezing, no similar improvement is observed for activated sludge. Moreover, curing affects neither sludge after liquid nitrogen freezing, but affects the slow-freezing activated sludge. © 2001 Elsevier Science Ltd. All rights reserved

Key words—sludge, freezing speed, dewaterability, curing, liquid nitrogen

INTRODUCTION

Freeze/thawing treatment, an effective sludge dewatering technique, has been extensively studied (see Vesilind and Martel (1990) and the references cited therein). The sludge dewatering efficiency generally decreases with an increasing freezing rate during freeze/thaw treatment. The freezing time is critical and instant freezing is found to be inadequate for improving sludge dewaterability (Randall *et al.*, 1975; Ezekwo *et al.*, 1980).

Lee and Hsu (1994) investigated freeze/thaw treatment on waste activated sludge at an average freezing speed of 40 mm/h (11 μm/s). Such treatment can reduce the sludge bound water content to 50%, and largely decreases resistance to drying and filtration. Hong *et al.* (1995) noted that some extracellular polymers (ECPs) were released from the sludge body when the freezing speed was low. Hung *et al.* (1996) comprehensively considered how freezing speed affects the dewaterability of activated sludge. These authors noted that at a low freezing speed (less than 6 μm/s), not only are the floc density and morphology considerably changed, but the sludge filterability and settleability are also markedly enhanced. Hung *et al.* (1997) noted that the correlation between the freezing speed and the activated sludge characteristics is independent of the geometry of the freezing chamber. Chu *et al.* (1999) adopted a freezing speed exceeding -50 K/s, or -3000 K/min. In this case, the microbial density levels in the sludge had not been effectively reduced although the sludge dewaterability remained unchanged. (Note: The freezing speed can be measured by the propagation speed of the ice front in the sample, in μm/s, or by the local temperature decline rate, in K/s. These two measures are equivalent if the sample size and thermophysical properties are already known.)

The above literature reveals the serious constraint imposed by freeze/thaw treatment on activated sludge: the freezing speed must be low enough to reach sufficient sludge conditioning. Parker and Collins (1999) used liquid nitrogen to condition the water treatment residuals through "ultra-rapid" freezing. These authors' conclusion, "ultra-rapid freezing with liquid nitrogen successfully conditioned an alum water treatment residual", contradicts the general consensus that sludge dewaterability can be improved only when the freezing speed is low enough. High-speed sludge freezing would be most beneficial if feasible as claimed by Parker and Collins (1999). Apparent contradictions exist, nevertheless, in the claims concerning the effects of freezing speed. To our knowledge, no comprehensive work has examined how high-speed freezing affects different sludges. This work examines the feasibility of using a "high-speed" freezing technique, using LN_2-freezing to condition activated sludges and water treatment residuals. The freezing speed reached 200 μm/s (0.72 m/h), which is much higher than those speeds found in most literature on sludge freezing, such as 20 μm/s in Uhlman *et al.* (1963); 3–23 μm/s in Logsdon and Edgerley (1971); 1.4–72.6 μm/s in Hung *et al.* (1996); and 25 μm/s in Parker and Collins (1999). The so-called "ultra-rapid" cooling adopted in low-temperature applications has exceeded 10^4 K/s

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(Echlin, 1992). Herein, we refer to the present freezing test as "high-speed" rather than "ultra-rapid" a term used by Parker and Collins (1999), to prevent confusion. The frozen samples were cured for up to 24 h in LN_2 or in a freezer at −20°C to demonstrate the effects of curing. The frozen samples were thawed in a water bath for 1 h.

EXPERIMENTAL

The samples

The waste activated sludge samples were taken from the wastewater treatment plant of the Neili Bread Plant, Presidental Enterprise Co.,. Taoyuan, Taiwan. Four sludge samples were sampled on different dates (denoted herein as sludge samples #1–#4) from the recycled activated sludge stream. The sediment of the original sludge was employed as the freezing sample after a 5 h settling, thereby largely eliminating effects of sedimentation. The weight percent of solids in sediments of samples #1–#4 were 1.0%, 0.42%, 1.6%, and 0.85%, respectively.

Two water treatment residual samples were taken from the Chaung-Shin Water Treatement Plant in Taipei City on different dates, and are referred to herein as samples #1 and #2, respectively. The raw water, whose turbidity is normally in the range 10–50 NTU, was treated by alum ($Al_2(SO_4)_3{\cdot}14H_2O$). Samples #1 and #2 are testing samples from 5 h settling sediment of alum sludge, with solid contents being 5.82% and 11.5% w/w, respectively.

Freeze/thaw treatment

LN_2-freezing was achieved using plastic containers of radius 4.25 cm and height 5.0 cm, containing sludge samples which were suddenly immersed into an LN_2 pool at −196°C for 3 min. Film boiling established on the sample surface gave an average heat transfer coefficient of $100\,W/m^2\,K$ (Hua and Liu, 1998). Experimental results indicated that 2-min LN_2 freezing was sufficient to completely freeze the sludge body. The sludge sample could be completely frozen in approximately 120 s, giving an average freezing speed of 200 μm/s. This result suggested that the time spent for water freezing was approximately 80 s.

Some samples were kept in the LN_2 pool following 3-min freezing for 2–24 h to examine the effect of curing. These sludges are called "LN_2-cured" (LC) sludges. Parker and Collins (1999) cured their samples at −10°C and demonstrated a marked improvement in dewaterability. Some samples after 3-min LN_2 freezing were immediately transferred to a freezer at −20°C for 2–24 h to illustrate the effect of curing temperature. These sludges are the "freezer-cured" (FC) sludges.

Some original sludge samples were directly placed in the −20°C freezer for 2–24 h (without LN_2 freezing) for comparison. Complete freezing was achieved within approximately 2 h. The curing time is thus between 0 and 22 h. These sludges are "slow-freezing" (SF) sludges.

All the above-mentioned freezing and curing testing schemes were applied to all samples, including two alum and four activated sludges.

Sludge tests

Capillary suction apparatus as described by Lee and Hsu (1993) was used to estimate the sludge filterability. The CST for original alum sludge samples #1 and #2 and activated sludge samples #1–#4 are 107, 303, 74, 80, 49 and 123 s, respectively. Particle size distribution (PSD) was determined with a particle size analyzer (Coulter LS230). Hindered settling tests were performed in tubes of diameter 1 cm and height 15 cm after sample thawing. The zone settling velocity (ZSV) was obtained by linear regression of the interface height versus time data for the constant-rate period, indexes sludge settleability (Chen *et al.*, 1996). The original alum sludge samples #1 and #2 exhibit ZSV's of 51 and 1.1 μm/s, respectively. The relatively low ZSV and comparatively large CST observed for alum sample #2 were probably due to the insufficient coagulation of particles in raw water by the failure of the alum dosing pump during the sampling period. The ZSV's for the original activated sludge samples were all essentially zero. The initial and the equilibrium sludge heights after 24 h of settling were recorded as l_i and l_f, respectively. For waste activated sludge, only a very slight settling took place (less than 2%). For alum sludge, however, 24-h settling yielded a further 50% lowering of the sediment. Some samples were placed in a funnel and subjected to 53.2 cm Hg vacuum filtration. The suction was turned off only when no further filtrate could be removed from the filter cake. The residual moisture in the filter cake is denoted as W_{FIL}. The values for alum sludges #1 and #2 and activated sludges #1–#4 are 1.5, 1.25, 10.4, 7.3, 8.6 and 17.5 kg/kg DS, respectively. Clearly, the present activated sludge sample exhibits a poor settleability and much bound water when compared with the alum sludge.

RESULTS AND DISCUSSION

Figures 1–4 depict the CST, ZSV, l_f/l_i and residual moisture content in the filter cake before and after treatment, for the alum sludge and for the activated sludge samples #1–#4. Among all samples, the SF sludge exhibits the greatest improvement in dewaterability, including filterability (much less CST), settleability (greater ZSV), and bound moisture content (lower l_f/l_i ratios and less W_{FIL}). This result closely corresponds to previous results (Lee and Hsu, 1994; Hung *et al.*, 1996).

The high-speed freezing using LN_2 quenching does not affect the dewaterability of alum sludge, including a reduction in CST (from 117 s to 40–50 s) and in l_f/l_i ratio (from 0.48 to 0.28). Moreover, the corresponding ZSV increases from 50 to around 70 μm/s. Namely, although the freezing speed adopted in the present work is much higher than that used in Parker and Collins (1999), the water treatment residual can still be conditioned to some extent. LN_2 freezing has a negligible effect on the activated sludge characteristics except in the CST. Restated, the ZSV, l_f/l_i, and W_{FIL} values remain unchanged after LN_2-freezing, suggesting that a freezing speed sufficient for conditioning the alum sludge is insufficient for conditioning the activated sludge. The type of sludge, as well as the freezing speed determines the sludge conditioning efficiency.

Figures 1–4 show that curing has no detectable effects on the conditioned sludge characteristics. The insignificant role of curing in freeze/thaw treatment contradicts the observations of Parker and Collins (1999), who postulated that curing caused a continuous loss of unfrozen moisture in the "pockets" in the frozen sludge. We could not observe the proposed "pocket" effects in our LN_2 freezing sludge.

Jean *et al.* (2000) demonstrated a marked curing effect on activated sludge when it was frozen and cured in a mechanical freezer at −17°C. As a control,

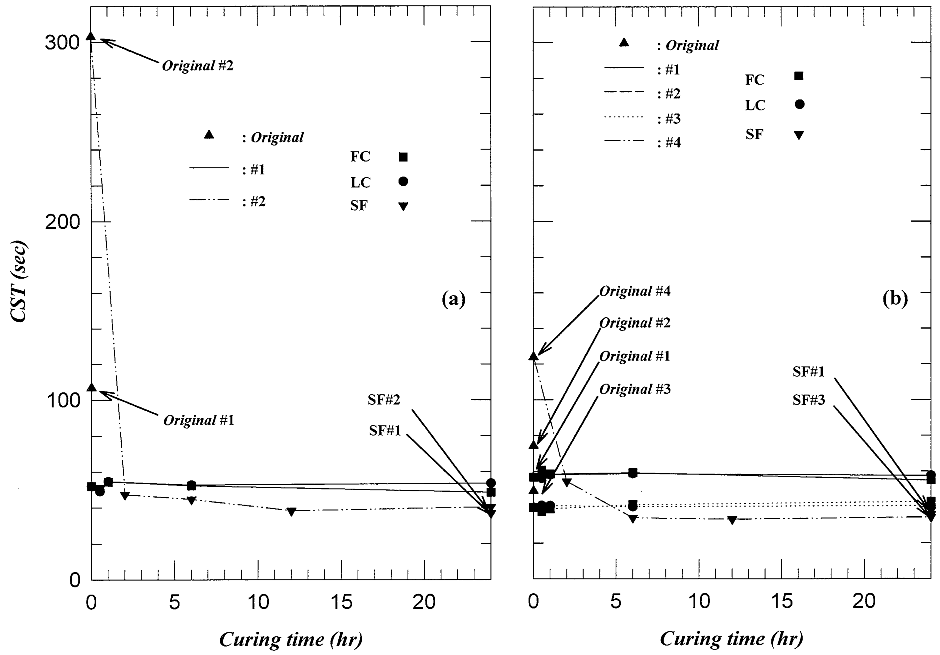

Fig. 1. Capillary suction time (CST) versus curing time. (a) Alum sludge: #1—LN_2-freezing, #2—SF sludge; (b) activated sludge: #1—#3—LN_2-freezing, #4—SF sludge.

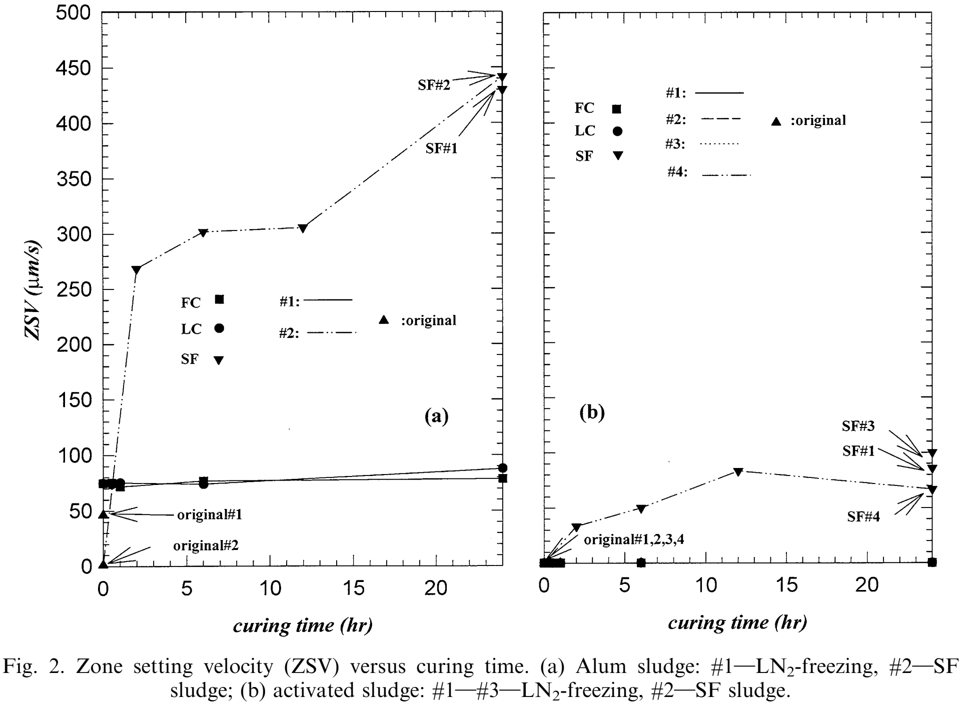

Fig. 2. Zone setting velocity (ZSV) versus curing time. (a) Alum sludge: #1—LN_2-freezing, #2—SF sludge; (b) activated sludge: #1—#3—LN_2-freezing, #2—SF sludge.

independent tests with activated sludge sample #4 frozen and cured in the −20°C freezer were conducted, and the results are presented in Figs 1–4. Notably, curing markedly affects the characteristics of the SF sludges. Restated, the effect of curing depends upon the manner in which the sludge sample is frozen. Curing has no effect with high-speed freezing (LN_2-freezing) but significantly enhances the sludge dewaterability with slow freezing.

Figure 5 shows the sludge floc diameter before and after freezing. The floc size of the SF activated sludge

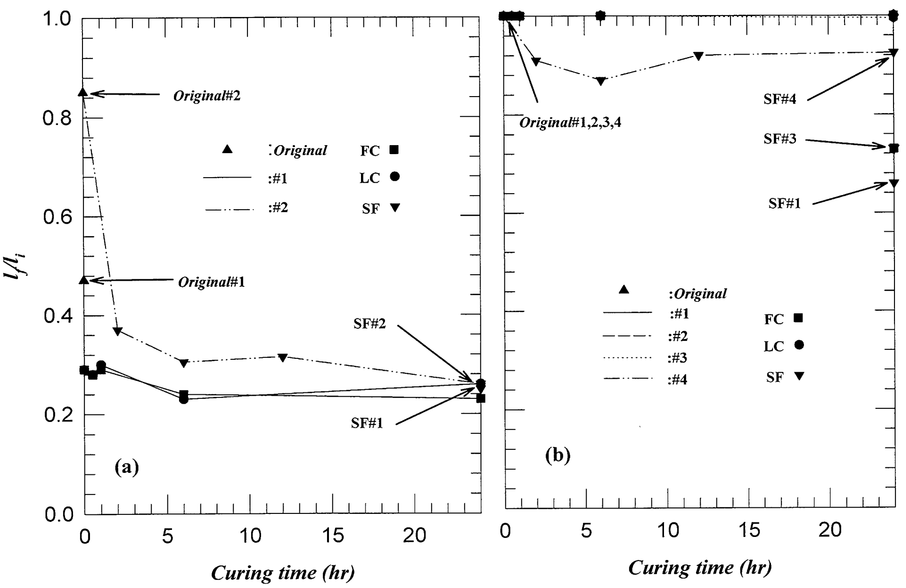

Fig. 3. Sediment height ratio (l_f/l_i) versus curing time. (a) Alum sludge: #1—LN$_2$-freezing, #2—SF sludge; (b) activated sludge: #1—#3—LN$_2$-freezing, #4–SF sludge.

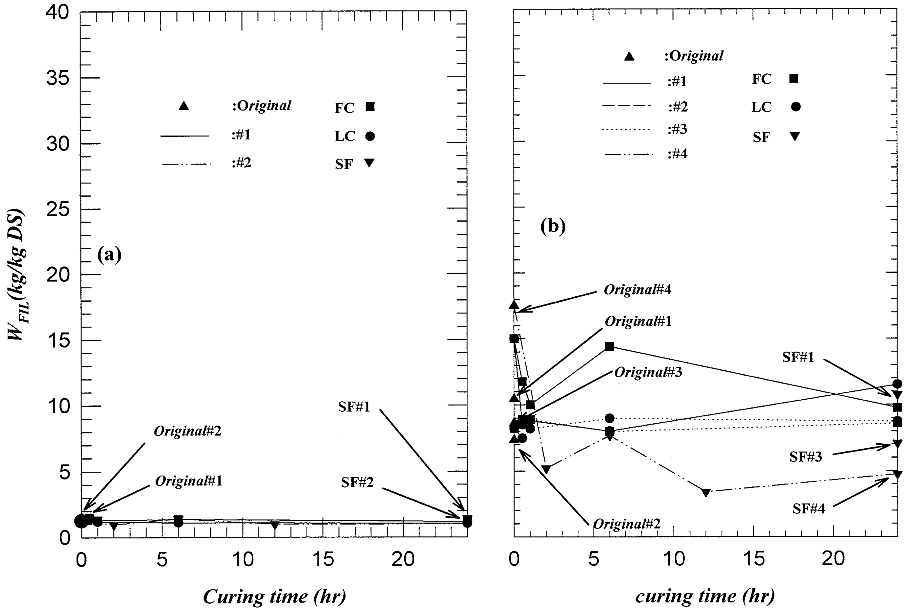

Fig. 4. Residual moisture content (W_{FIL}) versus curing time. (a) Alum sludge: #1—LN$_2$-freezing, #2—SF sludge; (b) activated sludge: #1—#3—LN$_2$-freezing, #4—SF sludge.

is noted to be much greater than that of the other samples. Slow freezing yields a "gross migration" of sludge particles in advance of the growing ice front, and produces large, compact flocs, and thus satisfactory dewaterability for SF sludge. After LN$_2$-freezing, the floc size d_f of alum sludge #1 decreases from 27 to 10–12 μm; this fact should be attributed to the action of the growing fingering ice front with fast freezing which tears up the original sludge flocs (Parker *et al.*, 1998). However, the change in floc size for activated sludge is negligible. The ice fingering could not effectively tear up the floc structure of the activated sludge.

Although the present freezing test could still improve alum sludge dewaterability, we believe that conditioning fails when the freezing speed still rises further. Vitrification of water in the sludge sample could occur under ultra-rapid freezing. All water molecules would be transferred into a glassy state such that no ice crystal could nucleate or grow during

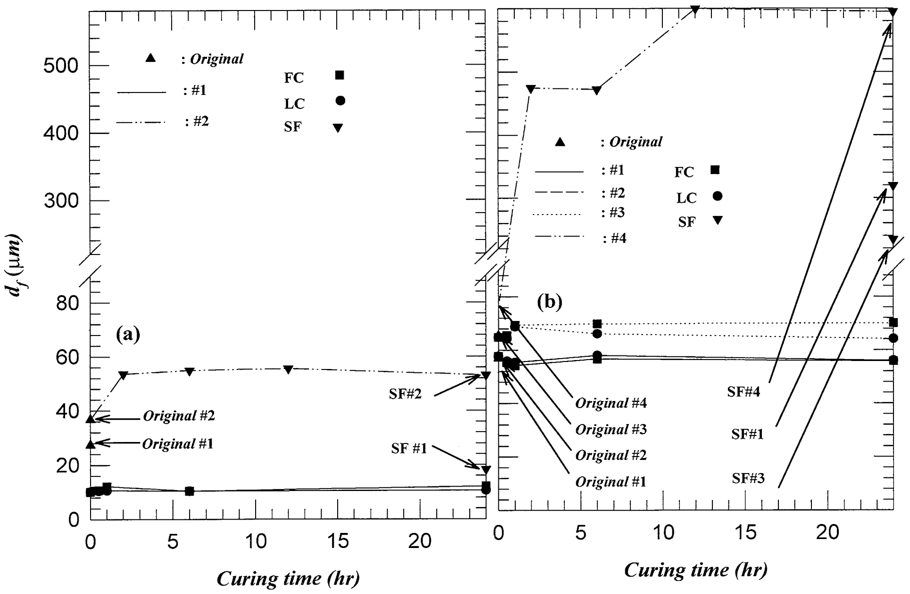

Fig. 5. Floc diameters (d_f) versus curing time. (a) Alum sludge: #1—LN_2-freezing, #2—SF sludge; (b) activated sludge: #1–#3—LN_2-freezing, #4—SF sludge.

freezing. The sludge flocs would thus remain intact after ultra-rapid freezing. This proposition also accounts for why the cryopreservation technique preserves cells and plant seeds for a long period (Kartha, 1985). We expect that the moisture distribution in the sludge, determining its dewaterability, would not be altered after ultra-rapid freezing. A sludge can only be sufficiently conditioned by recrystalizing glassy state ice during thawing. Different sludges achieve vitrification at different critical freezing speeds. Parker and Collins (1999) and the present test support the feasibility of using faster freezing than previously used to condition the alum sludge. However, this conclusion does not apply to activated sludge. In summary, we believe that "ultra-rapid" freezing cannot sufficiently condition sludge, and the present test was unable to provide a high enough freezing speed to induce vitrification of sludge water.

CONCLUSIONS

This work examined the feasibility of using liquid nitrogen to freeze alum sludge and waste activated sludge samples to imitate a "high-speed" freezing environment. The freezing speed reached 200 μm/s (0.72 m/h), much higher than speeds adopted in most earlier works on sludge freezing. The frozen samples were thawed in different manners. Sludge settleability, filterability, and floc sizes were measured before and after freeze/thaw treatment. Three minutes liquid nitrogen freezing led to improved filterability and settleability for alum sludge but not for activated sludge. Curing affects neither sludge after liquid nitrogen freezing, but altered the characteristics of activated sludge when frozen at a low speed.

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