Final Report

TREATMENT OF OIL CONTAMINATED SOIL FROM A WYOMING REFINERY

by

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August 18, 1995

An oily soil sample was shipped from the refinery site to the test Laboratories on June 17, 1995. The sample was stored at 4 °C until testing began. The sample was in the form of a dense pasty mud, black in color, and consisted of oily residues mixed with what appeared to be bentonite clay. Characterization showed the following:

Parameter	Content		
	% of orig. wt.	% of dry wt	mg/kg dry wt
Total solids	67.8		
Water	32.2		
Volatile solids (includes TPH)	10.3	15.2	
Ash	57.5	84.8	
Total Petroleum Hydrocarbons	4.52	6.67	66,700

The oily nature of the sample precluded adding it directly to test reactors because it could not be transferred easily and could not be suspended in cold water. To prepare the tests, the oily soil was suspended in hot water in the amount of 200 grams per liter of water. In some cases, Tween-80 was used as a surfactant at a T-80 to soil ratio (w/w) of 1:10 as recommended by Janiyani, et al. (*Chem. Tech. Biotechnol., 1993*). The final test characteristics of the soil suspension, T-80, and soil+T80 mixtures were as follows:

Sample	TCOD, mg/L	sCOD, mg/L	TSS mg/L	VSS, mg/L	TPH, mg/L
Soil + water	55,000	115	135,600	20,600	9,045
Tween-80 (10 g/L)	24,000	24,000			
T-80+Soil+water	83,500	24,115	135,600	20,600	9,045

The test program consisted of two sets of aerobic respirometer tests, one set of anaerobic semi-continuous reactor tests, three batch anaerobic tests, and one set of four bench-scale slurry reactors. The project was considered complete as of July 17 but respirometer tests were continued through August 15. An analysis of the test results is given below.

Aerobic Respirometer Tests

Aerobic respirometer tests were conducted on the following samples or sample combinations:

SET I	
2	Seed blank (50 mL activated sludge mixed liquor)
2	Control (Ethanol at 340 mg COD/L)
3	Soil suspension + T-80 (1, 2, 4 mL)
2	Tween 80 only (1 and 2.5 mL)
3	Soil suspension w/o Nutrients/Minerals (2.5, 5 and 10 mL)
2	Soil suspension + Nutrients and Minerals (5 and 10 mL)

Respirometer tests were conducted by adding the indicated volumes of test suspension to 250 mL respirometer vessels. The final volume was made to 250 mL by using distilled water along with nutrients, minerals, and buffer as indicated above. The vessels were then connected to an AER-200 respirometer system (Challenge Environmental Systems, Inc., Fayetteville, AR) for measuring oxygen uptake.

SET I tests results through 240 hours of incubation are shown in Figure 1 (Data are given in tabular form in Appendix B). Oxygen uptake data are reported as % of TCOD to provide a common basis for comparison. As indicated, the ethanol in the Control and the organic material in the Tween-80 sample both degraded with essentially 100% conversion. The soil+T80 showed a significantly lower oxygen uptake, but it should be recognized that the COD of this mixture was 83,500 mg/L. Subtracting the oxygen uptake for the T-80 sample from that of the Soil+T80 showed a negative oxygen uptake through 108 hours, but the rate increased at about the same as the T-80 thereafter. This respirometric oxygen uptake reaction indicates that the oily soil inhibited the T-80 biodegradation slightly, but recovery occurred with time. The two soil samples with and without nutrients and minerals showed essentially the same oxygen uptake averaging about 20% of the control after 10 days of incubation.

SET II consisted of continuation of some of the SET I tests along with additional reactors containing new oily soil sample as follows:

SET II		
CONT.	3	Soil suspension + T80 (1, 2 and 4 mL; Cont'd from SET I)
	2	Soil suspension + Nutrients and Minerals (5 and 10 mL; Cont'd from SET I; no commercial culture)
NEW	3	Soil suspension w/o Nutrients/Minerals (2.5, 5 and 10 mL; Cont'd from SET I+ 1 mL commercial culture[a]
	2	Soil + NM (5 and 10 mL new sample w/o seed)
	2	Soil + NM (5 and 10 mL new sample plus 1 mL commercial culture)
	2	5 and 10 mL commercial culture alone

[a] Commercial culture = MUNOX 112 from OSPREY Biotechnics, Sarasota, FL

The oxygen uptake data for SET II tests through 1026 hours (42.75 days) of incubation are shown in Figure 2 expressed as a percent of the COD. In this case, the COD used in the continuing samples was that remaining at the end of the SET I tests. All data have been corrected for the contribution from the seed culture. SET II test results indicated that the commercial culture did enhance the biodegradation of the organic material remaining from the SET I tests [Compare Soil(Cnt'd; no seed) with Soil(Cnt'd+Cult.) in Figure 2A] but did not enhance the rate of biodegradation of the organic materials in a new sample of the soil suspension. The sample receiving no seed organisms seemed to degrade with the same lag time, at the same rate, and to the same extent as the sample receiving the commercial culture (Figure 2B), indicating that the oily soil contained a substantial number of active microorganisms.

Long-Term Respirometer Tests

One sample set from the SET I tests containing soil+ Nutrients and Minerals and one sample set that received soil + T-80 also were continued through the SET II tests (see SET II table above). This test extension gave an opportunity to compare the effect of T-80 on a longer term basis. As indicated in Figure 3, the T-80 did seem to enhance both the rate and extent of biodegradation after an initial period in which the T-80 seemed to cause a reduction in oxygen uptake. (Note: This reduction in oxygen uptake in the adjusted data early in the test is likely caused by the difference in timing of oxygen uptake in the T-80 and the soil samples, that is, the soil delayed the biodegradation of T-80. However, the maximum rate of oxygen uptake and the adjusted total oxygen uptake after 52 days of incubation are considered to be valid indications of the reaction).

Anaerobic Semi-Continuous Reactor Tests

Anaerobic semi-continuous reactor tests were conducted on the following samples or sample combinations (mL/d of feedstock represent volumes of 200g/L test suspension):

2	Control (Ethanol feedstock at 5 and 10 ml/day)
3	Soil suspension+5, 10 and 15 mL/d of Ethanol feedstock
3	Soil suspension only (5, 10 and 15 mL/d)
2	Tween 80 solution only (5, and 10 mL/d)
3	Soil suspension + T-80 (2.5, 5 and 7.5 mL/d)
2	Soil suspension only (5 and 10 mL/d without seed)
2	Soil plus commercial seed culture (starting on Day 12)

These tests were conducted by first transferring 100 mL of active anaerobic culture from a laboratory scale master reactor plus 50 mL of mixed liquor from the anaerobic digester at the local wastewater treatment plant to 250 mL serum bottles. The test reactors were then operated by daily addition of the indicated amount of test sample to the reactors. Gas production was measured daily by using calibrated syringes.

Cumulative gas production through 21 days of incubation are shown in Figure 4. The control sample showed normal gas production. (Since these reactors were seeded partially with mixed liquor solids from the local wastewater treatment plant digester, the decreasing slope of the control curve over time represents the decrease in active biomass caused by washout of the initial seed culture). The oily soil plus ethanol showed a lower gas production rate (as indicated by the lower slope of the cumulative gas production line in Figure 4A, but when the soil COD was removed from the calculation, the gas production was in close agreement with the control (Figure 4B). This analysis shows that the oily soil caused a slight inhibition of ethanol degradation as indicated by the decreasing slope of the gas production curve between days 8 and 15, but recovery occurred rapidly after day 15. The fact that essentially no gas was produced in the sample receiving soil only (with and without seed addition) verified that the organic constituents of the oily soil were not readily biodegraded in the anaerobic environment used in the study. The T-80 only sample showed an initial low gas production rate but recovery occurred starting about day 6 and the rate of gas production began to parallel that of the control starting about day 11 (Figure 4A). Therefore, T-80 appeared to be anaerobically biodegradable, but some acclimation of the anaerobic culture was required. The soil+T80 sample showed relatively low gas production rate per unit of COD

(Figure 4A). Removing the oily soil COD from the calculation showed that the rate of the gas production from the sample equaled that of the control and the T-80 only samples (Figure 4B).

Batch Anaerobic Test Program

On days 3, 10 and 18 of the semi-continuous reactor tests, batch tests were conducted by measuring the gas production hourly through a 24-hr period using an automatic ANR-100 anaerobic respirometer (Challenge Environmental Systems, Inc., Fayetteville, AR). These tests verified the results of the semi-continuous tests (Figures 5A, B, and C). Data for day 3 shows that during the acclimation period, little gas production occurred in the samples containing soil only or soil + T80, and only the soil+ethanol reactor showed a significant amount of gas production. By days 10 and 18, all reactors except the one containing soil only showed gas production.

Aerobic Slurry Tests

Aerobic slurry tests consisted of adding the following oily soil combinations to each of four 10-L reactors similar to that shown in Figure 6:

Reactor	Feedstock Composition	Feedstock Concentration			
		TCOD	TSS .	nVSS	VSS
R1	Oily soil suspension	1,667	4,120	3,495	625
R2	Oily soil + Tween 80	2,530	4,120	3,495	625
R3	Tween 80 alone	730	0	0	0
R4	Oily soil + comm. Culture	1,667	4,120	3,495	625

These slurry reactors were fed on a draw and fill basis in which mixed liquor was removed daily and replaced with various fresh oily soil sample plus dilution water. The reactors were operated for 14 days at hydraulic and solids retention times of 4 days. This allowed the reactors to approach steady state operating conditions. Test parameters consisted of measuring volatile and total suspended solids and soluble COD in the reactor supernatant. (The feed plan for these reactors is given in detail in Appendix D).

Figures 7A, B and C show consistent trends in MLSS and MLVSS concentrations for all reactors. (Note: the low MLSS and MLVSS in the soil+culture reactor from days 10 through 13 for Reactor 4 were caused by insufficient mixing). As indicated, the MLSS levels varied between 2,500 and 3,500 mg/L (Figure 7A) while the MLVSS concentrations ranged from 500 to 600 mg/L (Figure 7B). The mixed liquor solids in the Tween-80 reactor ranged only from 100 to 200 mg/L because of the low non-volatile content of the feedstock. The difference between the MLVSS concentration in reactors receiving oily soil samples and the sample receiving only T-80 verifies the contribution of the inert but volatile constituents in the oily soil.

Soluble COD measurements for the slurry reactors are shown in Figure 7C. The reactors receiving soil only and soil+culture showed essentially the same sCOD throughout the test period. Since, the influent sCOD of the feedstock was only 115 mg/L and the effluent sCOD averaged 170 mg/L, the overall soluble COD removal efficiency was essentially 0%. The T-80 seemed to cause high soluble COD concentrations in the reactors receiving T80 alone or soil+T80. Subtracting the sCOD of the T-80 sample from that of the soil only sample would leave essentially no residual soluble COD. While, the evidence is limited, this results implies that T-80 helped to improve the removal of sCOD in the soil sample, which is consistent with the observations from aerobic respirometer tests (see Figure 3).

Total Petroleum Hydrocarbon Measurements

Total petroleum hydrocarbon (TPH) concentrations were measured in the original soil and in the mixed liquors and effluent from the slurry reactors. A summary of results is shown in the following table:

Sample	Sample TPH		
	mg/L	mg/kg soil (as received)	mg/kg soil (dry wt)
Oily soil		45,230	69,700
Reactor feedstock	275	45,230	69,700

Slurry Reactor	Mixed liquor TPH (mg/L dry wt)				
	Tot. TPH mg/L	Sol. TPH mg/L	TPH in Soil mg/L	MLSS, mg/L	TPH: mg/ kg TSS .
R1 (Oily soil only)	245	60.6	184	3,500	52,600
R2 (Oily soil + T80)	256	9.3	247	3,500	70,600
R3 (T-80 only)	60	39	21	100	
R4 (Oily soil + culture)	280	24	256	3,500	73,100

These data indicate that there was a slight (9 to 24%) removal of total petroleum hydrocarbons in the slurry reactors in terms of volumetric concentrations but not in terms of mg TPH/kg of dry weight in the soil and soil+culture reactors. There also was little evidence that the commercial culture caused improved biodegradation of TPH. However, operation of all reactors for longer times and at higher solids retention times possibly could improve the biodegradation of hydrocarbons. The low reduction in volumetric TPH in the reactor receiving Tween 80 mixed with the soil is thought to be caused by the contribution of T-80 to the measured TPH.

CONCLUSIONS

Aerobic and anaerobic treatability tests on the Refinery oily soil showed the following:

1. The removal of total COD was low and at best approached 40% with no additives to about 70% when using Tween 80 as an amendment.
2. Anaerobic tests showed essentially no conversion of COD to methane gas.
3. Total petroleum hydrocarbons did not seem to be biologically degraded in short-term aerobic slurry reactors, and the soil solids removed from the reactor had essentially the same TPH/kg dry solids as did the original oily soil. However, operation for longer times and at higher solids retention times might allow improved biodegradation of hydrocarbons.
4. Addition of nutrients and minerals did not seem to accelerate the rate or increase the extent of biodegradation of organic materials in the oily soil.
5. Addition of a commercial hydrocarbon-degrading culture did not accelerate the rate or increase the extent of biodegradation of the organic constituents of the oily soil. However, longer test times or use of other cultures might have improved the biodegradation.

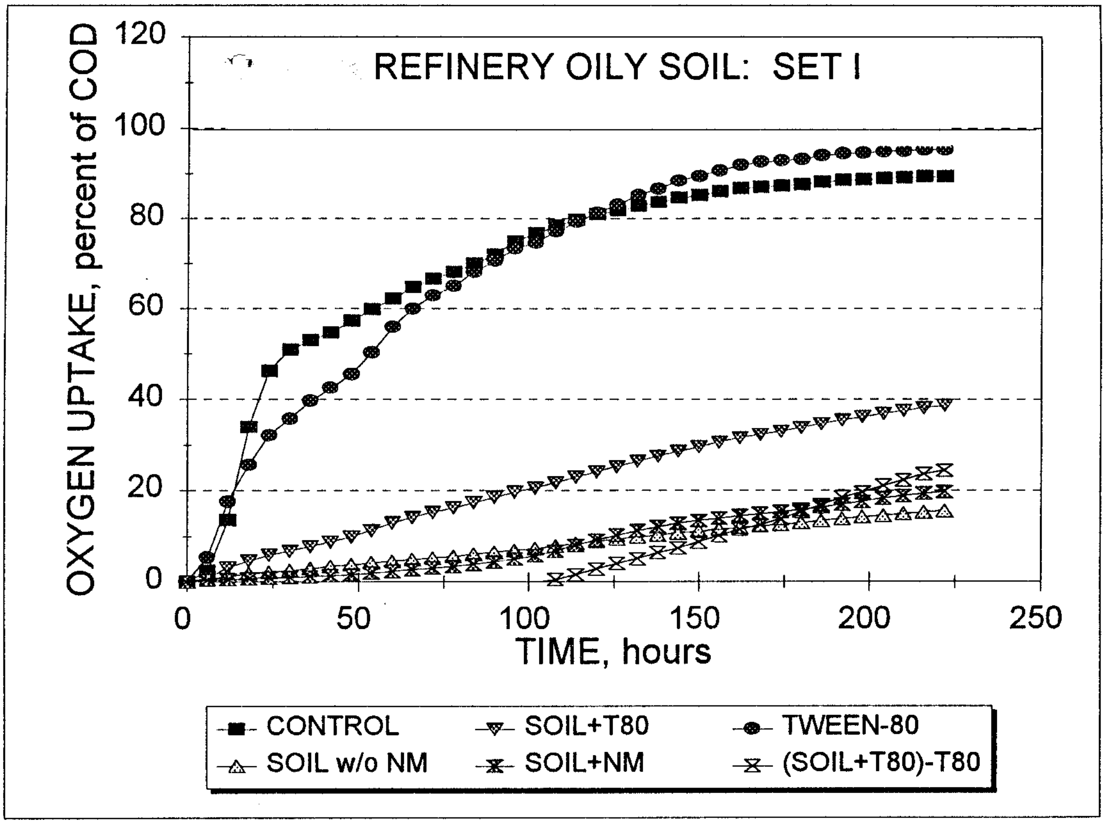

Figure 1. Oxygen uptake for aerobic respirometer test SET I.

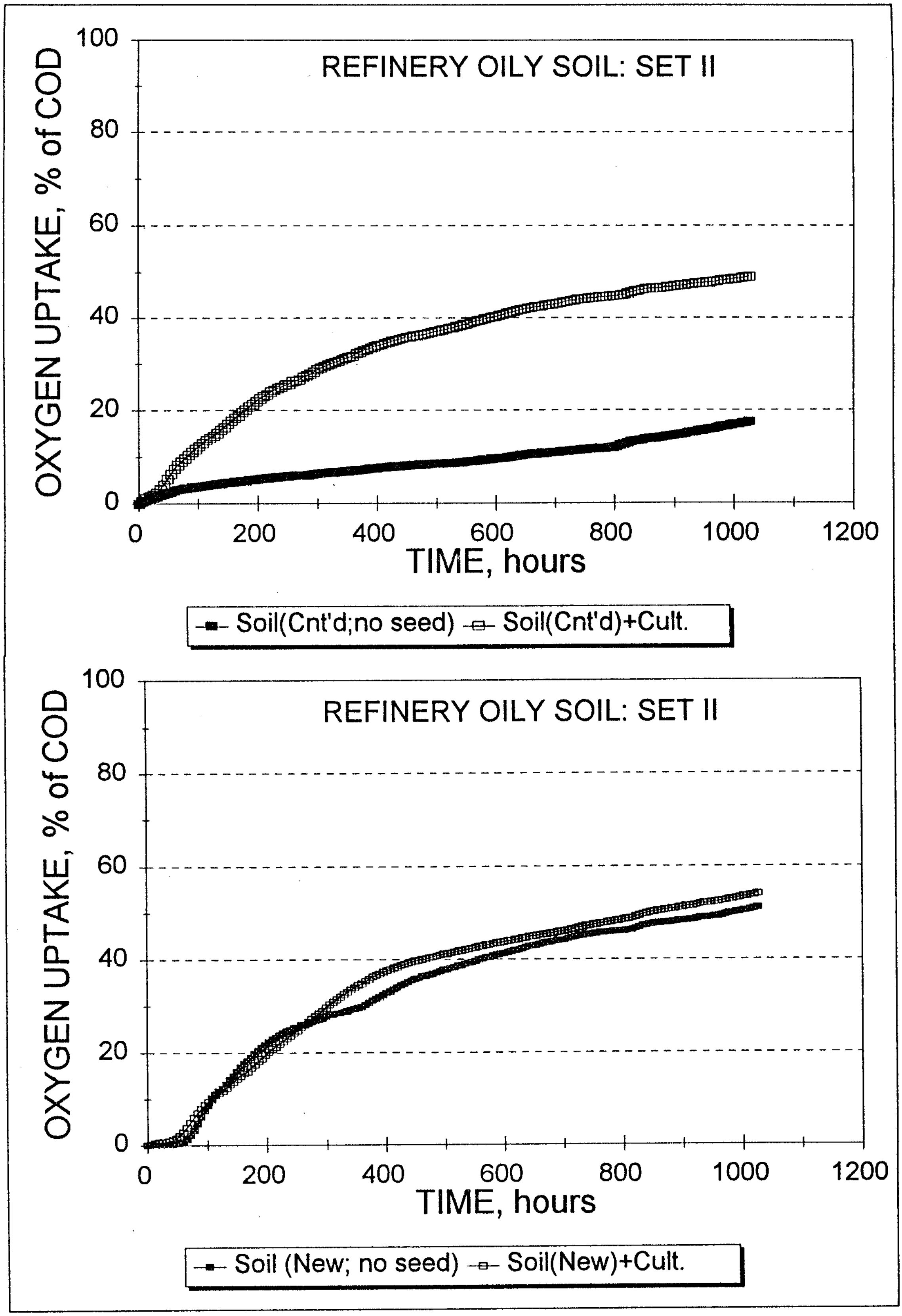

Figure 2. Oxygen uptake for SET II aerobic respirometer tests for tests continued from SET I (A) and tests with new sample(B).

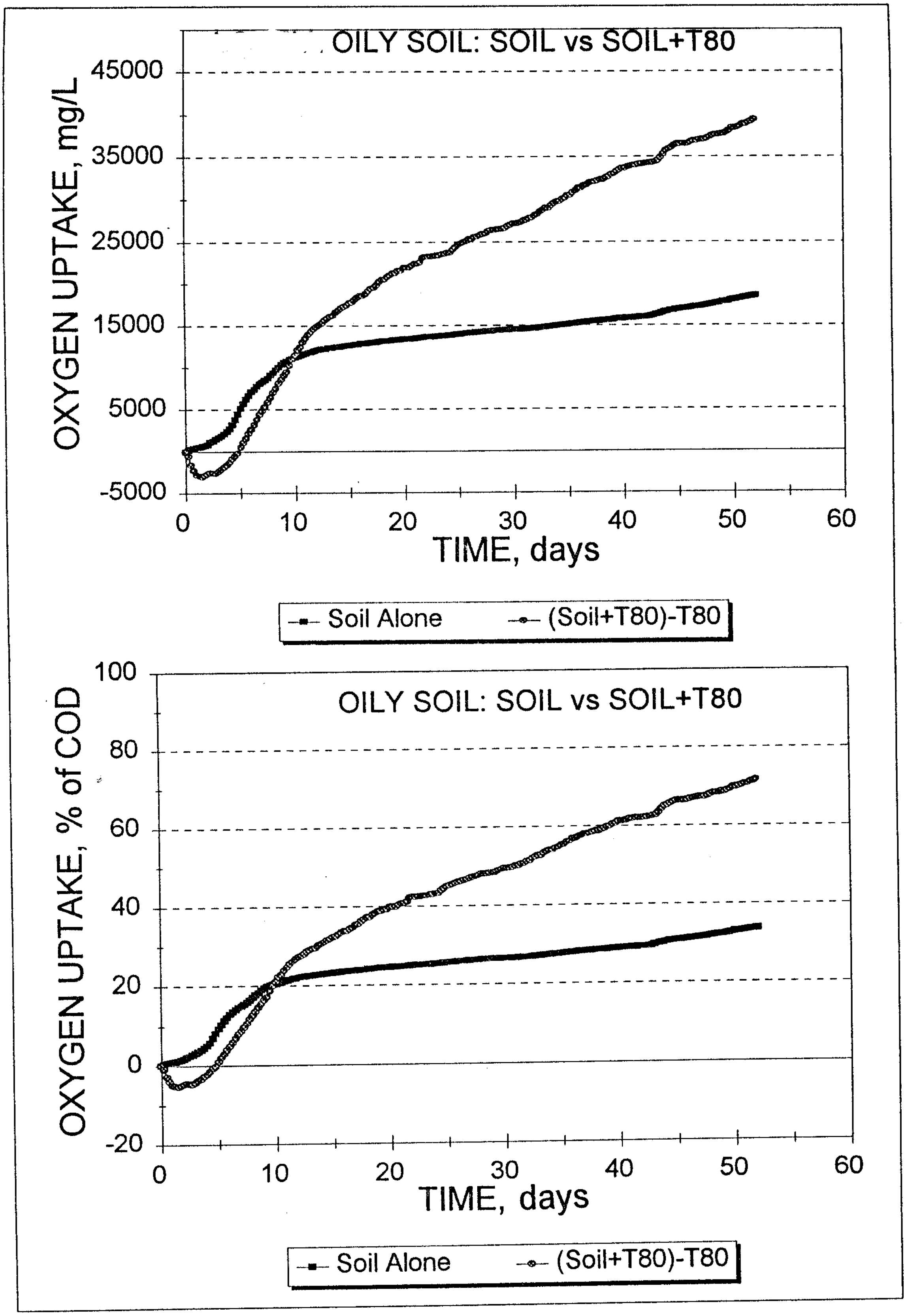

Figure 3. Oxygen uptake expressed in mg/L (A) and as a percent of COD (B) for reactors containing oily soil only and oily soil plus Tween 80.

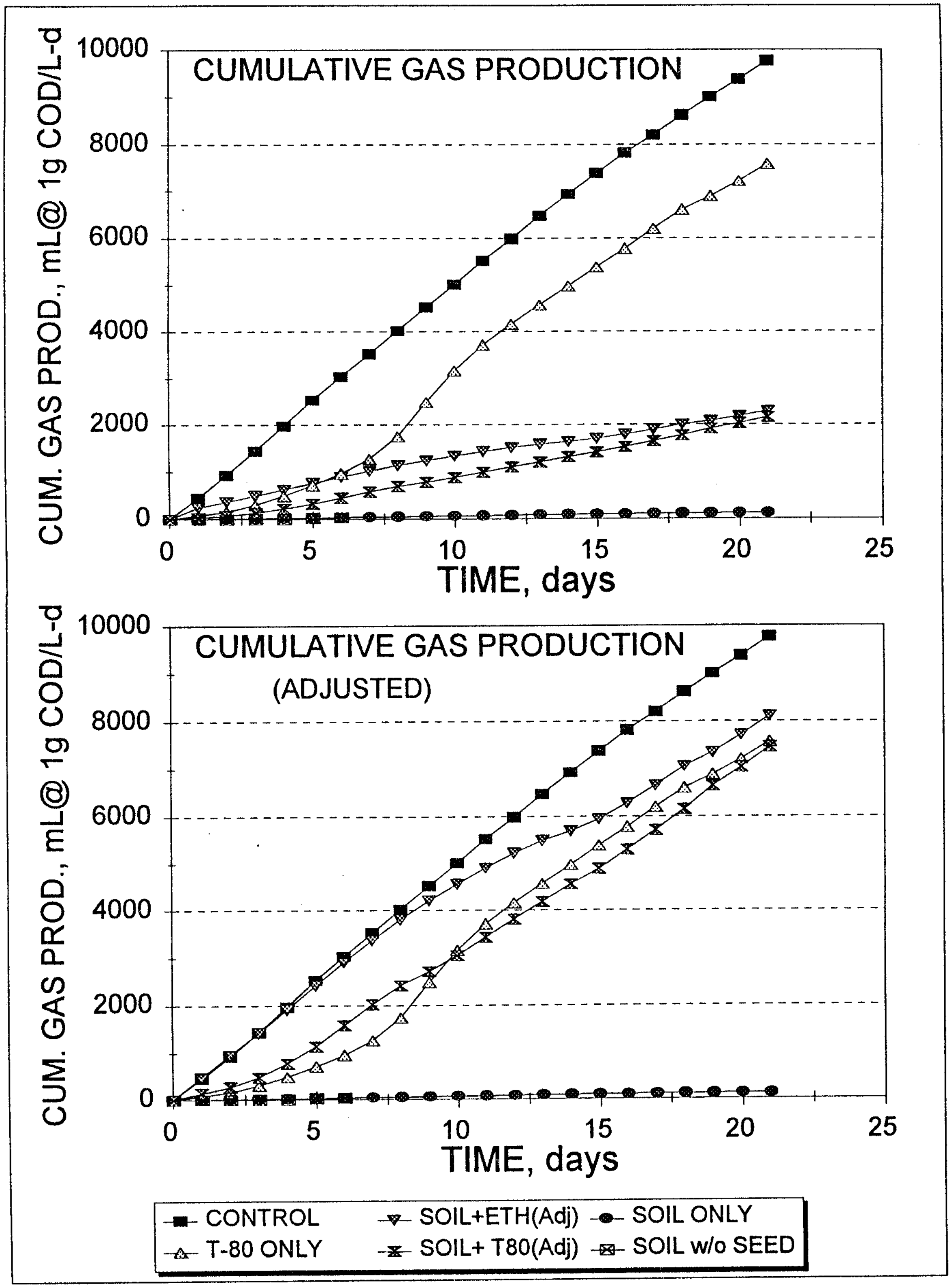

Figure 4. Cumulative gas production in anaerobic test reactors showing results of direct measurements (A) and after adjusting the gas production of the soil+ethanol and soil+T80 samples for the contribution of the oily soil to the sample COD (B).

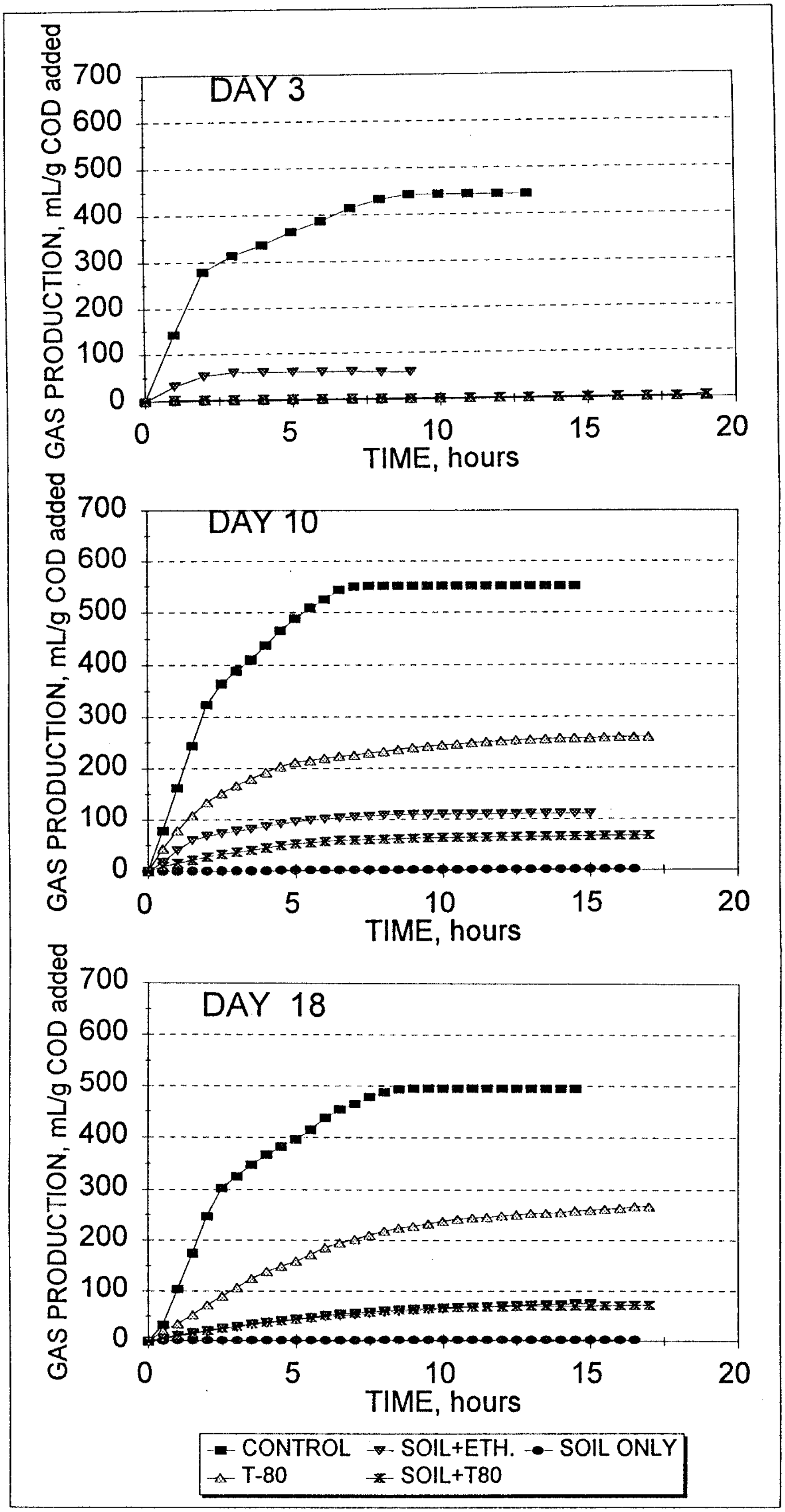

Figure 5. Hourly gas production on Day 3 (A) Day 10 (B) and Day 18 (C) of the semi-continuous anaerobic reactor tests.

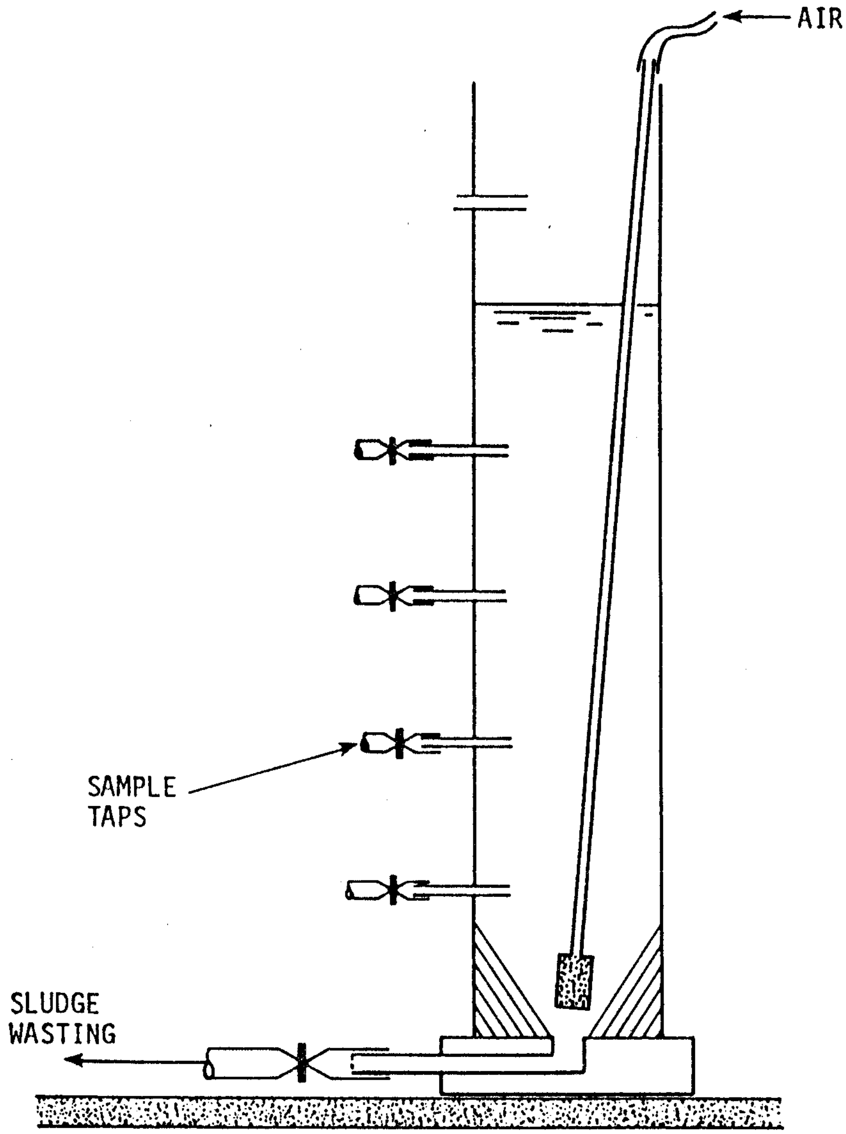

Figure 6. Schematic diagram of the test apparatus used for the aerobic slurry reactor tests.

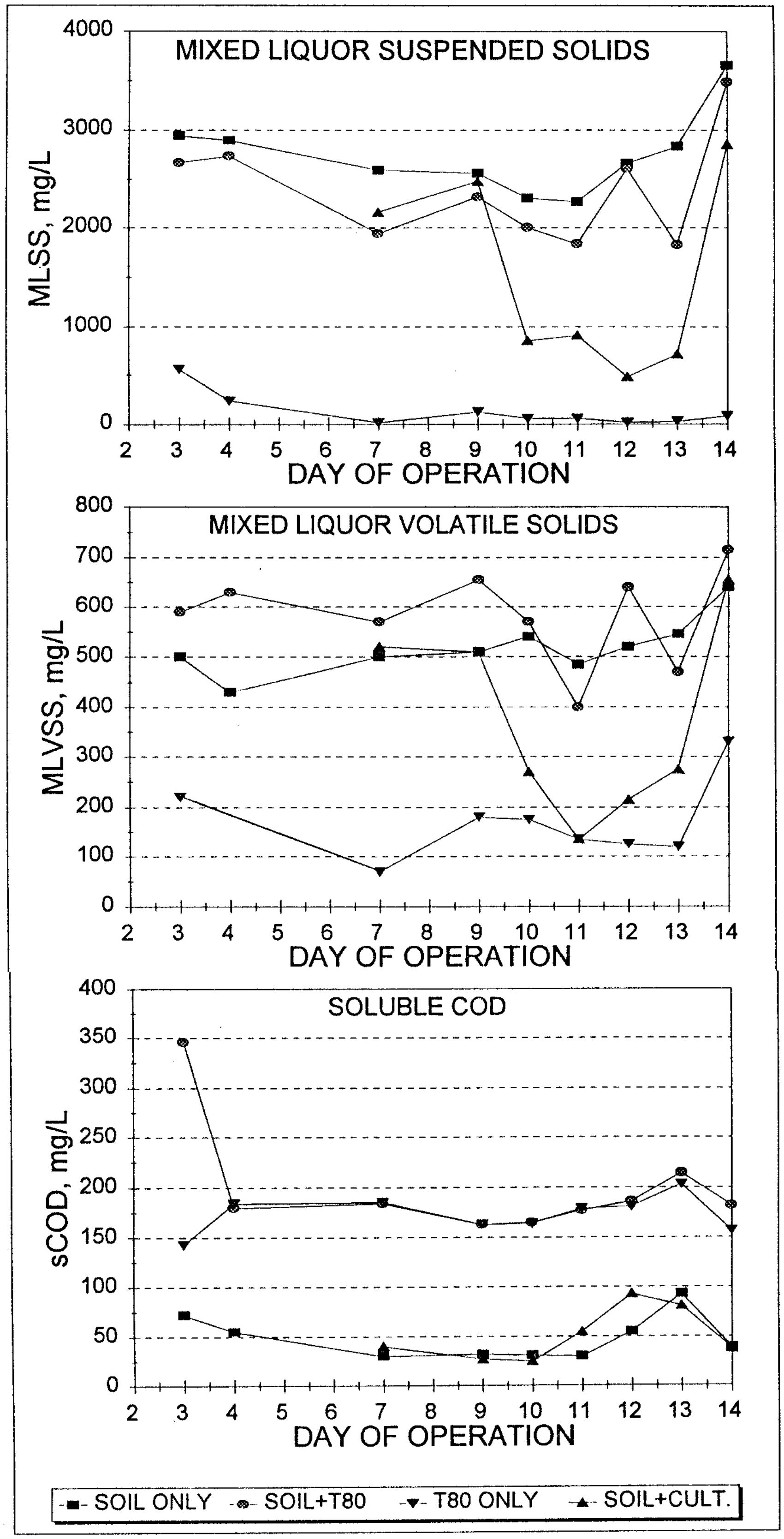

Figure 7. Mixed liqour solids (A), mixed liqour volatile solids (B), and soluble COD (C) for the aerobic slurry reactors.