

Trichloroethylene sorption and oxidation using a dual function sorbent/catalyst in a falling furnace reactor

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Received 21 July 1997; received in revised form 20 February 1998; accepted 24 February 1998

Abstract

A dual function zeolite medium (Cr-ZSM-5), capable of physisorbing trichloroethylene (TCE) at ambient temperature and catalytically oxidizing it at elevated temperature ($\sim 350^{\circ}\text{C}$), was utilized in a novel continuous falling furnace reactor system to store and periodically destroy this chlorinated volatile organic compound.

For inlet feed streams between 50 and 1600 ppm of TCE in humid air, overall destruction levels were typically above 99%. Also, since the falling furnace system required heating only during the desorption/reaction portion of the process (5–10% of the cycle time), energy comparison with conventional catalytic reactors is extremely favorable. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Sorption; Adsorption; Catalysis; Zeolites; VOCs; Oxidation; Remediation

1. Introduction

Chlorinated volatile organic compounds (CVOCs) have been produced commercially and used for many purposes by the chemical industry including the manufacture of herbicides, plastics, and solvents. Uses outside the chemical industry include solvent degreasing in the automotive and aerospace industries, dry cleaning solvents in the garment industries, and solvent cleaning in the electronic industries. Soil and ground water contamination due to improper disposal of the CVOCs has become a major concern. One

process that is used to alleviate ground water contamination is a combination of stripping the CVOCs from the ground water using air and then oxidizing the CVOCs in the air to relatively non-hazardous compounds such as carbon dioxide (CO_2), water (H_2O), and hydrochloric acid (HCl).

The major methods of destruction of these compounds are thermal and catalytic destruction with catalytic destruction favored economically because of the lower temperatures necessary to destroy the CVOCs. Catalytic destruction normally requires temperatures below 500°C , which is much lower than the above 1000°C used for thermal incineration. Another advantage of catalytic destruction is the potential for excellent selectivity toward the formation of non-hazardous reaction products. Both processes require

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heating a large stream of air to reaction temperature which is energy intensive even with heat recovery. Thus, there is an urgent need to develop a more energy efficient process that will convert these compounds to relatively non-hazardous materials.

The development of a new, novel, patented [1] energy efficient process to convert CVOCs to CO_2 , H_2O and HCl is described. The process is based upon the use of a proprietary dual function sorbent/catalyst medium developed by Greene and coworkers [2–5]. It is based on either the ZSM-5 or Y zeolites. At ambient conditions, the medium acts as a selective adsorbent for the CVOC in the presence of high water vapor concentrations. Then, when the medium is raised to reaction temperature (250–350°C), it is an effective and selective deep oxidation catalyst for the CVOCs. For example, at 350°C and a 2400 h^{-1} space velocity, the catalyst normally oxidizes more than 99.4% of the CVOCs.

Greene and coworkers [6,7] report that the adsorptive capacities at ambient conditions (15–25°C) and atmospheric pressure of this dual function sorbent/catalyst medium range from 5% to 10% by weight of CVOCs in the presence of 10 000 to 15 000 ppm water in the air for CVOC concentrations ranging between 100 and 1500 ppm. This capacity is sufficient to potentially make it attractive for commercial applications.

The use of supported transition metal oxides and precious metal catalysts for environmental remediation of CVOCs has previously been reviewed in the literature by Spivey [8]. More recently, work by others [9] has stressed the commercial potential of these catalyst systems in environmental control. Agarwal et al. [10] used a commercial chromia–alumina catalyst for deep oxidation of chlorinated hydrocarbons in the presence of water vapor. The catalyst contained about 9% chromia which is much higher than the levels in the zeolites used in this work. They found excellent catalyst stability when running the catalyst at 360°C for approximately 233 days. Their catalyst had a Cl_2 selectivity of less than 5%. Also, this catalyst produced some chlorinated hydrocarbons.

Previous work at The University of Akron [5,6,11] using exchanged Y zeolite and ZSM-5 zeolite based catalysts for deep oxidation of CVOCs showed the high activity and versatility of these media for one and two-carbon CVOCs, both saturated and unsaturated,

by using a variety of exchanged cations. Material balances, generally between 90% and 105% for both carbon and chlorine, showed oxidation selectivity to be primarily to CO_2 and HCl for humid feeds at temperatures below 400°C. Above 400°C there was increasing Cl_2 formation. No chlorinated organic products were detected, however. It was also concluded that the low cation levels (<1%) necessary in the exchanged zeolites would mean less environmental impact when they are eventually spent and require remediation/recycling themselves.

In this paper, the initial process studies using a falling furnace reactor packed with the dual function medium are described. The process studies were performed to demonstrate the ability of a dual function sorbent/catalyst to oxidize CVOCs and determine whether further process development was warranted. In this process, a moist air-CVOC mixture is passed through a single dual function sorbent/catalyst bed unit at temperatures ranging from 15°C to 30°C until the bed capacity, as determined from prior experiments, has been reached. Then the sorbent/catalyst bed is heated beginning at the effluent end and progressing toward the entrance using a moving furnace. The effluent end of the reactor is raised to the reaction temperature before significant quantities of CVOC are desorbed. When the initial portion of the bed is heated to reaction temperature, the furnace is lowered at a rate that will allow the CVOC that is desorbed to be completely oxidized. As the furnace travels down the bed, the rate of furnace movement is increased because of the increased amount of medium at reaction temperature. When all the CVOC has been desorbed, the furnace is raised and the bed is cooled rapidly by the incoming gas stream. This process cycle is repeated as necessary. The only time the bed is heated is during the desorption/reaction portion of the cycle. Even though the CVOC sorption capacity of the sorbent/catalyst medium is lowered from ~8% for a 1000 ppm feed to ~4% for a 100 ppm feed, the sorption period is lengthened by more than a factor of 4. Thus, the ratio of time at ambient temperature to time at elevated temperature in the cycle increases with decreasing CVOC feed concentrations. Typical sorption times ranged from ~1000 min for a 600 ppm TCE feed to ~2600 min for a 100 ppm feed, while desorption/reaction times ranged from 117 to 159 min depending upon the heating cycle used.

2. Description of work

A falling furnace reactor system was built and operated using a range of CVOC feed concentrations (50–500 ppm) and moisture contents (11 000–13 000 ppm). The moisture concentrations and the lower CVOC feed concentrations are near those that would be encountered in typical commercial applications. The other process variables studied were the adsorption temperature, time of adsorption, and bed heating profile. All adsorption work was performed at a space velocity of 600 h^{-1} based upon the total sorbent/catalyst bed and ambient conditions for the gases. The desorptions were performed at the same space velocity except for run 57, which was made to determine the effect of the desorption/reaction space velocity on the effluent CVOC concentration.

Fig. 1 is a schematic drawing of the unit. The reactor was constructed from 19 mm i.d. quartz tubing and mounted in the support structure. The furnace was mounted on wheels and the furnace unit attached to a travelling screw that was turned using a reversible, variable speed, constant torque Bodine drive to raise and lower the furnace. The drive unit had a lower speed of $1/3 \text{ RPM}$ and an upper speed of about 5 RPM .

The CVOC feed was prepared by passing a small stream of dry air, 1–4 ml/min, through a bubbler, which contained the CVOC, trichloroethylene (TCE). Moist air was prepared by passing 200–400 ml/min air (the amount depended upon the desired moisture concentration) through another bubbler filled with water. These two streams, along with the main air stream of 200–400 ml/min, entered the sorber/reactor at the bottom, passed through a plug of glass wool to mix the three streams, and then into the sorbent/catalyst bed. The air flow rates were controlled using needle valves after the compressed gas pressure was lowered to between 5 and 10 psig (34–70 kPa) using a two stage compressed gas pressure regulator. Feed samples were taken from between the glass wool plug and the bottom of the reactor bed using a 200 μl Hamilton gas-tight syringe, model CR-700-200. Product samples were taken from the top of the sorber/reactor system using another 200 μl Hamilton gas-tight syringe. A heating tape was wrapped around the top of the reactor and the side arm to prevent condensation in the effluent section of the reactor system.

Three thermocouples (Ts) were buried in the bed near the centerline: T 1 at the top of the bed, 0 cm (only one or two pellets covered it); T 3 in the middle

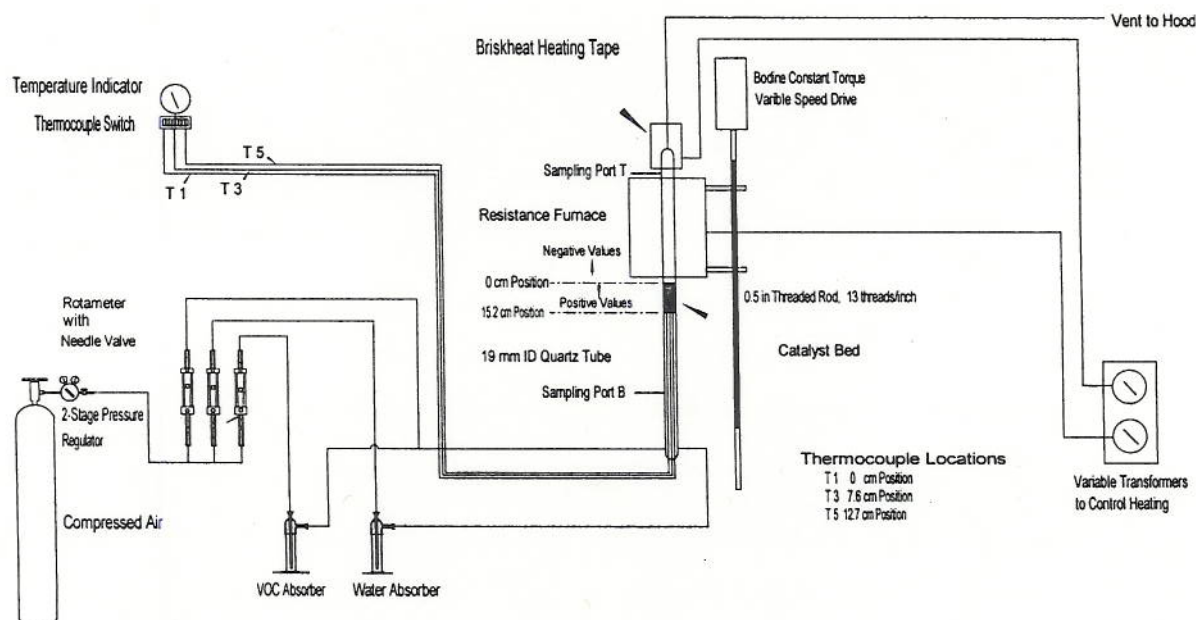


Fig. 1. Falling furnace sorption/reaction unit schematic.

of the bed, 7.6 cm from the top of the bed; and T 5 12.7 cm from the top of the bed. A total of 60 cm³ of a Cr-ZSM-5 sorbent catalyst was placed in the unit which gave a bed length of 15.2 cm. Physical properties of the fresh and used (after ~50 sorption/oxidation cycles) sorbent/catalyst are given in Table 1. Table 2 gives the fresh catalyst activity for TCE oxidation.

The feed and product gas streams were analyzed for TCE and CO₂ using a Hewlett-Packard gas chromatograph model 5890 equipped with a mass spectrometer (MS) detector model 5970. A 12 m×2 mm Hewlett-Packard Ultra 1 capillary column coated with a 0.33 mm film of methyl silicone gum was used to separate the gaseous components. This particular instrument had a lower detection limit of about 10 ppm TCE for a 100 µl sample injection. The CVOC peak elution time was about 1 min, so that samples could be drawn from the column every 2–3 min. The time to charge the syringe was less than 10 s. The CVOC calibration curves for the GC-MS were prepared by injecting a known amount of reagent grade TCE into a 1 liter dilution flask and allowing the flask

contents to mix for at least 20 min. For a 2015 ppm TCE concentration, 8 µl of reagent grade TCE was injected into the dilution flask. The calibration curve was prepared by drawing 3 to 5, 100, 75, 50, 25, and 10 µl samples from the flask and injecting them into the GC-MS. If high concentrations of CVOC (>2000 ppm) were expected, then a series of 200 µl injections were added to the curve. The preparation of the calibration curve was repeated weekly or whenever the instrument parameters were changed by the autotuning process.

During the sorption phase of the process, the bottom of the furnace was above the catalyst bed and the power turned off. When the desired amount of CVOC had been passed through the bed, the bottom of the furnace was lowered to the desired initial position and the power turned on. Two initial positions were used: 2.5 cm above the top of the bed, and 2.5 cm below the top of the bed. The unit was allowed to sit at this position for a period of time, and then the furnace was lowered at a pre-selected rate to raise the bed temperature to desorption and reaction temperatures. Table 3 shows the position, Powerstat settings, screw speed (rotational), relative power usage for the cycle, and the time of each stage for the four lowering profiles that were used. The relative power usage for each cycle was estimated by numerically integrating the square of the voltage times the time at that setting for the cycle and comparing the value to the initial cycle.

Each heating run had minor variations from those shown in Table 3. These variations were primarily in the setting of the end time, because either the effluent TCE had not yet dropped to zero or CO₂ evolution was still detected.

3. Results and discussion

Four CVOC feed concentrations (~500, ~250, ~100, and ~50 ppm) were used to develop the data presented in Table 4. Table 4 gives the ambient temperature, heating cycle, the TCE feed concentration, the space velocity, the average reaction concentration, the amount of CVOC adsorbed to the start of desorption/reaction, the total CVOC fed during the run, the TCE percentage conversion, the maximum outlet concentration, the duration of the run, the heating

Table 1
Catalyst properties

Parameter	Fresh	Used ^a
Support	ZSM-5	ZSM-5
Particle diameter (cm)	0.16	0.16
Particle length (cm)	0.48	0.48
Cation, Cr ⁺³ (%)	0.60	0.59
Surface area (m ² /g)	344	306
Acidity, mg NH ₃ /g catalyst	17.4	17.8
Crystallinity ^b (%) (Reference H-ZSM-5 ^c)	94	85

^aCatalyst after ~50 sorption/desorption reaction cycles.

^bFrom X-ray diffraction data.

^cZeolite as received from manufacturer before chromium exchange.

Table 2
Cr-ZSM-5 catalyst activity for trichloroethylene oxidation

Temperature (°C)	TCE feed concentration (ppm)	Conversion (%)	Cl ₂ /HCl ratio	CO/CO ₂ ratio
350	1098	99.4	0.20	2.59
325	1162	98.9	0.09	4.79
300	1162	95.5	0.02	7.60
275	1067	75.8	0	14.5
250	921	48.9	0	37.4

Table 3
Desorption/reaction heating cycles

Heating cycle	Time ^a (min)	Furnace position ^b (cm)	RPM	Powerstat setting	Relative power use ^c
1	–30 to –10	–2.5	0	90	1.00
	–10 to –2	–2.5	0	60	
	–2 to 2	–2.5–2.5	5	60	
	2–12	2.5	0	60	
	12–72	2.5–6.5	1/3	60	
	72–125	6.5–15.7	1/3	60	
2	0–20	2.5	0	90	0.833
	20–70	2.5–6.5	1/3	60	
	70–125	6.5–15.7	1	60	
3	0–20	2.5		80	0.890
	20–40	2.5–3.8	1/3	80	
	40–90	3.8–7.1	1/3	60	
	90–129	7.1–15.7	1	60	
4	0–40	2.5	0	80	1.10
	40–110	2.5–7.1	1/3	60	
	110–140	7.1–15.7	1.4	60	

^aTime from turning power on.

^bFrom top of bed, negative values are above the bed.

^cPower used overall for heating relative to cycle 1.

time, and the percent time that the total cycle is heated. The average reaction concentration was calculated by dividing the total CVOC fed by the amount of gas flowing during the desorption/reaction portion of the cycle. The lowest feed concentration was a compromise between obtaining reasonable run lengths with acceptable analytical precision, and the need to demonstrate the process in the region of expected commercial operations which often will be between 10 and 25 ppm. The total CVOC adsorbed on the catalyst bed ranged from less than 0.3 to >1.6 g. While the largest amount adsorbed was only a third of the saturation values for similar sorbent/catalysts developed by Greene and coworkers [5,6], the levels of absorption were not unexpected because the feed concentration of CVOC was much lower than that used in previous studies and the bed could not be saturated if high CVOC conversions were to be obtained. To ensure 99.9+% CVOC oxidation, the upper portion of the bed must remain CVOC-free for the initial heating and the contiguous region below must be only partially saturated because this is the location of the mass transfer zone.

During the initial work with this reactor, the optimal space velocity was found to be 600 h^{-1} , and that value was used for the sorption portion of the cycle and also for the desorption/reaction portion of the cycle except in Run 57. This space velocity was determined by the desired adsorption time and not by the amount of catalyst required for deep oxidation of the TCE. Others in our group, have shown that much higher space velocities can be used with this sorbent/catalyst during the sorption portion of the cycle without TCE leakage, and during the desorption/reaction portion of the cycle while maintaining greater than 99% conversion at temperatures of about 400°C . In an actual run, the space velocity based on the heated portion of the sorbent/catalyst bed at the beginning of the desorption/reaction cycle will actually be at least eight times the overall value shown above. The space velocity based on heated sorbent/catalyst will continually decrease during the run approaching 600 h^{-1} quoted above.

In Run 57, the space velocity during the desorption/reaction portion of the cycle was lowered to 297 h^{-1} . The data in Table 4 have been ordered from the lowest

Table 4
Summary data for falling furnace reactor

Run	Amb. temp. (°C)	Heat. cycle	Feed conc. (ppm)	Sorption sp. vel. (h ⁻¹)	Average reaction conc. (ppm)	TCE adsorbed to power on (g)	Total TCE (g)	Conversion (%)	Max outlet conc. (ppm)	Run duration (min)	Desorption/Reaction time (min)	Heating time(%)
<i>Low sorption group</i>												
52	12	1	52	608	484	0.18	0.20	100.0	0	1190	118	9.92
80	23	3	58	611	550	0.24	0.26	100.0	0	1357	132	9.73
47	20	1	65	608	634	0.25	0.28	100.0	9	1320	122	9.24
92	24	3	69	594	905	0.35	0.38	99.9	4	1608	119	7.40
81	23	4	100	592	745	0.35	0.39	100.0	0	1240	149	12.02
94	22	3	54	611	1130	0.51	0.54	98.6	49	2872	132	4.60
51	13	1	144	608	1518	0.57	0.66	99.5	25	1376	122	8.87
87	21	3	172	641	1710	0.68	0.76	99.7	13	1210	117	9.67
55	16	1	80	608	1637	0.69	0.72	99.3	23	2715	123	4.53
75	22	3	1533	615	3006	0.75	1.43	100.0	0	285	131	45.96
91	20	3	237	613	2057	0.75	0.88	99.8	16	1073	119	11.09
54	16	2	194	613	1971	0.77	0.88	95.8	293	1095	123	11.23
45	21	1	289	608	2219	0.81	0.95	96.6	238	1020	119	11.67
61	18	1	208	612	2339	0.89	1.00	99.9	15	1361	118	8.67
<i>Middle sorption group</i>												
66	22	3	306	608	2180	0.95	1.02	83.9	1495	1207	131	10.85
59	16	2	265	615	2252	0.98	1.09	46.5	2578	1247	134	10.75
71	22	3	271	612	2057	1.02	1.11	97.7	232	1266	150	11.85
89	22	3	113	611	2296	1.07	1.12	97.3	182	2752	135	4.91
70	23	2	278	595	2901	1.07	1.19	99.7	23	1243	117	9.41
53	12	2	270	608	2796	1.10	1.24	84.7	1070	1379	124	8.99
82	23	4	301	618	2239	1.11	1.23	95.0	806	1264	151	11.95
57	20	1	303	603	3157	1.14	1.29	94.4	1171	1280	115	8.98
64	23	2	285	613	2836	1.14	1.24	50.4	2801	1343	121	9.01
99	21	3	310	606	2252	1.24	1.27	99.8	22	1400	158	11.29
63	23	2	329	603	2674	1.25	1.34	76.2	2460	1281	141	11.01
<i>High sorption group</i>												
44	21	1	273	608	4002	1.30	1.58	99.3	148	1102	110	9.98
77	22	3	404	604	4093	1.47	1.60	98.9	250	1253	110	8.78
65	23	2	392	585	3744	1.52	1.55	85.1	1614	1307	120	9.18
68	22	3	420	608	3140	1.59	1.79	63.5	1931	1332	159	11.94
93	26	3	539	612	5110	1.63	2.25	90.0	2754	1126	122	10.83
58	22	1	431	615	4117	1.67	1.83	69.0	5522	1395	123	8.82
79	23	3	429	613	3859	1.76	1.95	82.0	3679	1402	140	9.99

to the highest amount of TCE fed during the sorption period. In addition, the table has been separated into three groups of runs, referred to as low, middle, and high sorption. Carbon and chlorine material balances could not be performed because of the time required to sample the exit stream for CO and Cl₂ using Dräger tubes and for HCl by water absorption during the transient heating cycle. Parallel work by others [5–7] in this group with similar catalysts operating under steady state conditions showed that the material balances could be closed.

The physical properties for the catalyst, as shown in Table 1, changed during the operation of the system. While the total chromium content did not change significantly, the crystallinity of the sample and the surface area decreased by about 10%. This indicates that the used catalyst is more amorphous than the fresh catalyst. The measured acidity increased slightly although not significantly as the catalyst aged.

For the low sorption group, the average fractional conversion of TCE was over 99.3% except for Run 45 which was an early run for which a good heating profile had not been developed and which had the highest amount of TCE adsorbed in this group of runs. Run 91 had a maximum TCE exit concentration of about 16 ppm, which occurred immediately after the furnace had reached its lowest position. This late peak in the exit CVOC effluent concentration indicates that the amount of CVOC being desorbed from the bed at that time was greater than the amount that could be converted by the catalytically active portion of the bed. A slightly smaller furnace lowering rate would have eliminated this peak. The overall TCE conversion for this run was 99.8% and the percentage of desorption/reaction time for the total cycle was 11.1%.

For this group of runs, the percentage of the desorption/reaction time to the total cycle time varied from 46% for the highest feed concentration (1533 ppm) to 4.5% for the lowest feed concentration (80 ppm). A zero for the maximum outlet TCE concentration in Table 4 means that the concentration was below the detectable limits throughout the run. CVOC concentrations approaching the detection limit (~10 ppm) will have a high relative uncertainty. While the actual peak CVOC concentrations entering the reaction zone will be well above the average reaction concentration given in Table 4, these values provide a way of comparing the runs for the overall

TCE load on the catalyst. In this low sorption series of runs, the range of average TCE reaction concentrations varied from 484 to 3006 ppm. In Run 61, the conversion was 99.9% with an average reaction concentration of 2339 ppm which means that a sufficient portion of the upper section of the bed was at the reaction temperature before significant amounts of TCE were desorbed. It also indicates that the bed system should be capable of handling more than 0.89 gm of TCE fed in Run 61 before the heating portion of the cycle is started.

The middle group of runs had conversions ranging from 46.5% to 99.8%. Major differences among the fractional conversions were found in this series of runs. The average TCE reaction concentrations as defined above ranged from 2057 to 3157 ppm. Runs with lower fractional conversions were associated with differences in the way the bed was heated early on during the desorption/reaction portion of the cycle and also with the amount of TCE adsorbed when the desorption/reaction part of the cycle was initiated. Again, in this group of runs, the percentage of desorption/reaction heating time to the total cycle time decreased as the feed concentration was lowered. Over half of the runs had conversions greater than 94% with the largest being 99.8%. Heating Cycle 3 (Table 3) gave the best results of the four cycles used for this group with three out of five runs having conversions greater than 97% and one at 99.8%. Fig. 2, Run 70, shows a typical concentration, temperature, position history for one of the high conversion runs of this group. It should be noted that the time axis shows only the heating time and not the long ambient temperature sorption time. For this run, the heating time was 117 min while the sorption time was 1126 min.

In Run 64, the CVOC effluent concentration rose to over 2500 ppm early in the heating and remained there for over half of the desorption/reaction time. It then fell slowly to zero near the end of the heating portion of the cycle. The temperature, T1, did not reach 350°C until 58 min into this portion of the cycle. This means that the portion of the bed heated to reaction temperatures was insufficient to provide high TCE conversion for the quantity of CVOC that was being desorbed for the majority of the heating time. From Fig. 2 (Run 70), it is noted that the temperature T1 reached 350°C after only 38 min, or approximately 20 min earlier than in Run 64. This increased

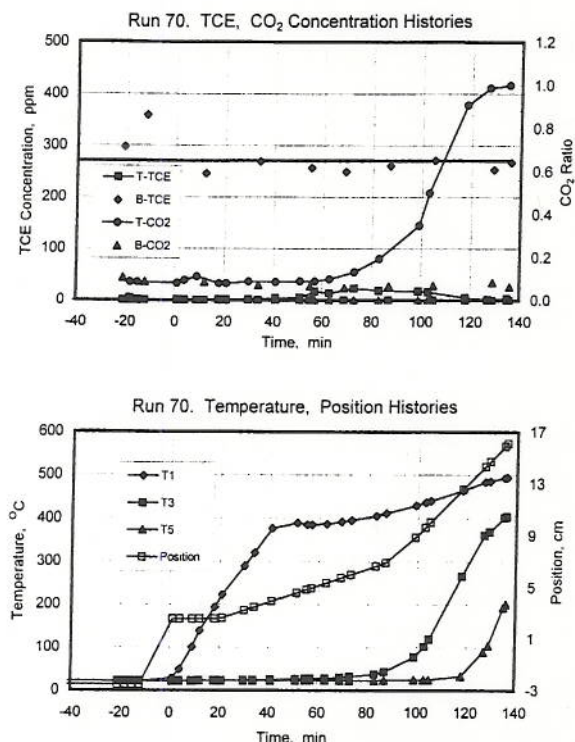


Fig. 2. Falling furnace sorbent/catalyst results: Concentration, temperature and position histories during desorption/reaction portion of the cycle ($SV=595\text{ h}^{-1}$; TCE feed=278 ppm; overall TCE conversion=99.7%; sorption time=1243 min; desorption/reaction time=117 min).

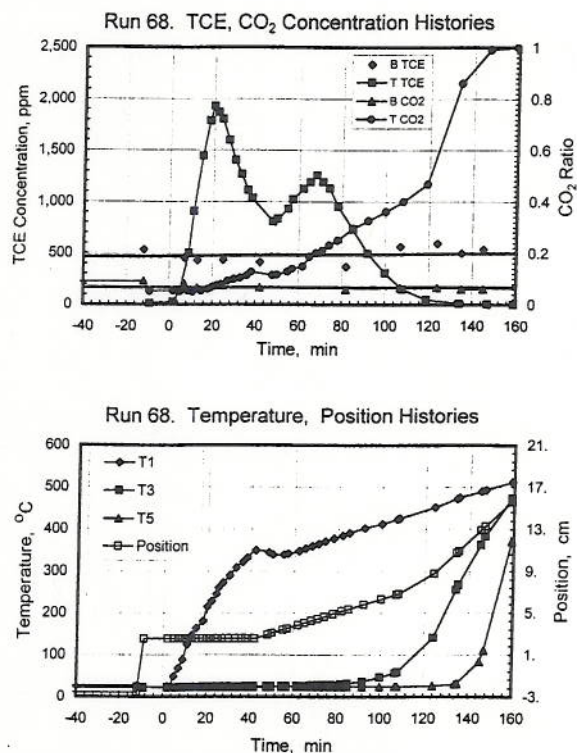


Fig. 3. Falling furnace sorbent/catalyst results: Concentration, temperature, and position histories during desorption/reaction portion of the cycle ($SV=608\text{ h}^{-1}$; TCE feed=420 ppm; overall TCE conversion=63.5%; sorption time=1332 min; desorption/reaction time=159 min).

temperature at the top was achieved by keeping the furnace stationary for 20 min at the start of the heating cycle and using a higher Powerstat setting. The furnace was then lowered at the same rate as in Run 64. This change in rate of temperature rise in the bed explains the lowering of the maximum effluent concentration from 2501 ppm for Run 64 to 23 ppm for Run 70. The percentage conversion for Run 70 was increased to 99.7% from 50.4% for Run 64.

The group of runs with the largest amounts of TCE absorbed had conversions ranging from 63% to over 99%. The conversion for the majority of runs in this group was below 90%. Fig. 3, Run 68, shows a typical concentration, temperature, and position history for a low conversion run from this group, while Fig. 4, Run 77, shows concentration, temperature, and position history for a high conversion run. From Fig. 4, it is seen that the effluent TCE concentration increased to

about 1900 ppm early in the cycle, indicating early desorption before the upper portion of the sorbent/catalyst bed reached catalytic temperatures. It then decreased to about 800 ppm and thereafter increased again to about 1250 ppm. This increase in concentration was caused by the lowering of the furnace before the upper portion of the bed was at reaction temperature. Not until the upper temperature, T 1, reached 375°C (about 70 min into the desorption) did the effluent TCE concentration rapidly fall.

Fig. 4 shows that the effluent TCE concentration increased early in the run to about 250 ppm which was about half the feed concentration, continued at this level for about 20 min, and then fell off rather quickly to below detection limits. When looking at the temperature curves for the two runs, it is noted that it takes much longer for Run 68 to reach the same temperature at a given position than for Run 77. The faster

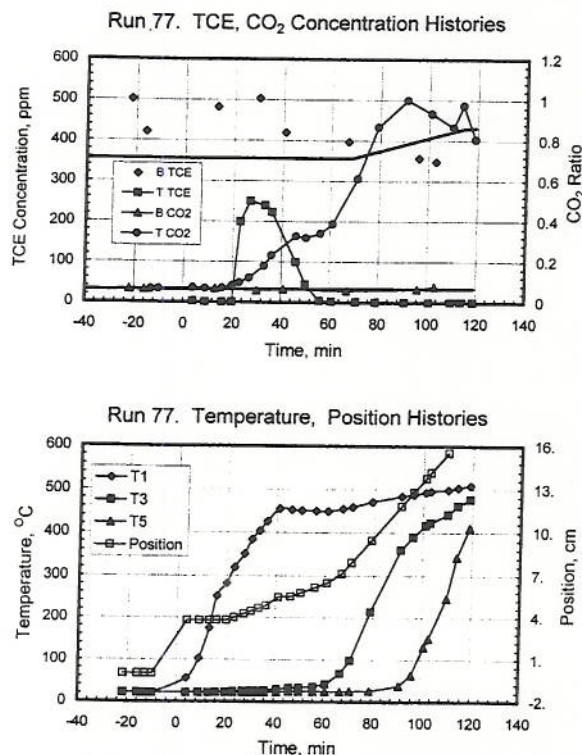


Fig. 4. Falling furnace sorbent/catalyst results: Concentration, temperature, and position histories during desorption/reaction portion of the cycle (SV=604 h⁻¹; TCE feed=404 ppm; overall TCE conversion=98.9%; sorption time=1,253 min; 0 desorption/reaction time=110 min).

temperature rise for Run 77 was caused by the higher furnace power levels. Thus, for Run 68, there was not sufficient sorbent/catalyst at the catalytic temperatures to convert the TCE that was being desorbed to CO₂, H₂O, and HCl. Alternately, the furnace position profile could have been changed to allow the upper section of the bed to reach a higher temperature before lowering the furnace and then lowering it more slowly until sufficient sorbent/catalyst had reached the reaction temperature. At that time, the furnace lowering speed could be increased.

The CO₂ concentrations are shown as the ratio of the instantaneous value to the maximum value because the response areas during the latter part of the run were much higher than those for which the GC/MS instrument was calibrated. While the CO₂ results are therefore qualitative, they help us to understand the final portion of the desorption cycle more completely. In all

cases, the maximum CO₂ concentration was found at the end of the desorption/reaction period. This would be expected because the bottom section of the bed is the last to be heated, and this is the portion of the bed that is most heavily saturated with CVOC. Also, the upper portion of the bed is at its highest reaction temperature (above 400°C) where equilibrium favors the production of CO₂.

In Figs. 2–4, it is noted that the temperature for T 1 was above 450°C at the end of the heating cycle. This means, based on equilibrium, that there were larger amounts of chlorine produced in this unit than would be desired. This high temperature was the result of the type of resistance furnace used. In a commercial unit or the next demonstration unit, the heating would be zoned so that the largest heat fluxes would be in the region that is being raised to desorption and then reaction temperatures. The heat flux for the rest of the bed would be reduced to that necessary to offset the heat losses to the surroundings. In this way, the maximum temperature in the reactor could be controlled below the temperatures that produce large quantities of chlorine. Also, there was a significant drop in effluent temperature (>20°C) after all the TCE had been desorbed and the sorbent/catalyst was being regenerated for another run. This indicates that the reacting TCE will provide part of the energy necessary to raise and maintain the gases and reaction zone at the reaction temperature.

These results show that the falling furnace sorber/reactor is able to maintain overall TCE conversions above 99% over a wide range of feed concentrations and bed loadings by appropriate adjustments in ambient sorption time, furnace drop rate, or power level. Alternate heating configurations involving sequential heat transfer zones, which would eliminate all moving parts in this process, are currently being investigated.

4. Catalyst stability

In a separate study in our laboratory, several chromium exchanged sorbent/catalysts were aged using ~1100 ppm TCE and ~13 000 ppm H₂O in air at 600°C for about 12 days with a space velocity of 2400 h⁻¹. Periodically, the temperature was lowered to 275°C and the sorbent/catalyst activity was measured. The use of higher temperatures during the

Table 5
Cr-ZSM-5 sorbent/catalyst properties for fresh and aged catalysts^a

Property	Fresh	Aged	Change (%)
Number of Al atoms/unit cell	4.8	4.8	0
Si/Al ratio	19	19	0
Cr (%)	1.03	0.84	18
Cr atoms/unit cell	1.1	0.9	18
Cr ³⁺ exchange ^b (%)	70		
Surface area (m ² g ⁻¹)	373	341	9
TPD acidity (mmol NH ₃ g ⁻¹)	1.34	1.14	15
TPD peak temperature (°C)	179 and 367	132 and 359	
NH ₃ molecules/Al atom	1.7	1.4	18
Relative crystallinity (%)	100	85	15

^aSorbent/catalysts aged at 600°C for 12 days at 2400 h⁻¹ using ~1100 ppm TCE, ~13 000 ppm H₂O in air.

^bBased on three Al atoms per Cr³⁺ cation.

deactivation work was necessary because at temperatures between 275°C and 400°C, activity decreases were so small that extremely long times were required to obtain a measurable activity decrease. This procedure was developed to reduce the time required for the deactivation experiments to reasonable lengths so that comparisons could be made among the sorbent/catalysts that were prepared using different supports, cations, and procedures for introducing the cations to the support.

Table 5 shows the characteristics of a fresh and aged Cr-ZSM-5 sorbent/catalyst that was prepared using the same procedure and substrate as the sor-

bent/catalyst used in the above experiments. While there were significant changes (>10%) in chromium content, relative crystallinity, and TPD acidity, the activity level at 275°C only decreased from 99% to 97% TCE conversion over the 12 days. The temperature of 275°C is lower than that used in the experiments reported in this paper and is lower than the expected operating temperature in a commercial unit. However, the low temperature was necessary to obtain conversions that were less than 100% during the deactivation runs. Fig. 5 shows the percentage TCE conversion obtained for a deactivation run length of 12 days. Twelve operating days of deactivation is equivalent to at least 144 desorption/reaction cycles for the sorber/reaction operation considered in this paper. This is equivalent to almost three years of operation if one assumes a seven day operating cycle (which is probably conservative at the expected CVOC feed operating levels). In actuality, the sorbent/catalyst could probably be used for a much longer period, because the operating temperatures will be between 300°C and 400°C rather than 600°C so that the rate of deactivation of the catalyst will be considerably lower than that shown in Fig. 5.

5. Energy consumption considerations

The fraction of ambient adsorption time to total run time ranged from 88% for the higher concentration

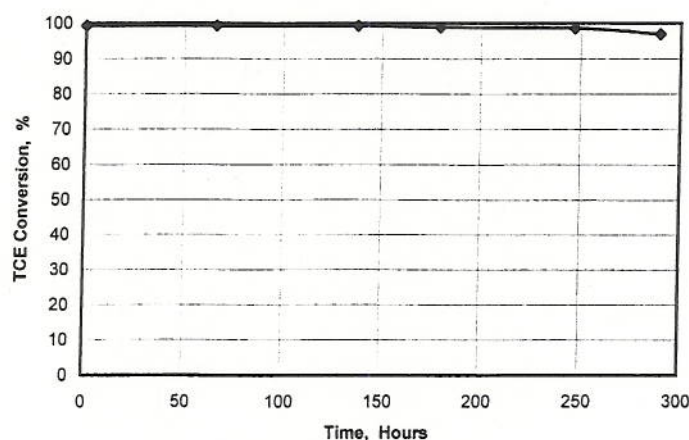


Fig. 5. Cr-ZSM-5 sorbent/catalyst TCE deactivation. Operating parameters: feed, ~1100 ppm TCE and ~13 000 ppm H₂O in air; space velocity, 2400 h⁻¹; catalyst aged at 600°C; TCE conversion measured at 275°C.

Table 6
Estimated energy usage and percent reduction

	Conventional reactor	Sorber/reactor
Feed concentration, Run 91 (ppm)	237	237
TCE to desorption (g)	NA ^a	0.75
Energy consumption (arbitrary units)	367	63.2
Energy reduction (%)	0	82.8
Heating time/cycle time (%)	100.0	13.5
Feed concentration, Run 55 (ppm)	80	80
TCE to desorption (g)	NA	0.72
Energy consumption (arbitrary units)	986	63.5
Energy reduction (%)	0	93.6
Heating time/cycle time (%)	100.0	5.8
Feed concentration (ppm)	20	20
TCE to desorption (g)	NA	0.72
Energy consumption (arbitrary units)	3756	63.5
Energy reduction (%)	0	98.3
Heating time/cycle time (%)	100.0	1.5

^aNot applicable.

feeds (~500 ppm) to over 95% for the lower concentration feeds (~50 ppm). This includes the furnace preheat time as well as the desorption/reaction time and is for a non-optimized sorption/reaction cycle. Further changes in the operating profile and methods are certain to decrease the preheat and desorption/reaction time compared to the total cycle time.

Table 6 presents an estimate of the relative amount of thermal energy that would be used by a conventional reactor without heat recovery versus the falling furnace sorber/reactor operated using the heating cycles for Runs 55 and 91. The projected energy savings are based only upon the energy (sensible heat) required to raise the feed stream from ambient temperature to reaction temperature. The conventional process requires heating for the whole cycle while the sorbent/reaction process is heated only for the relatively brief desorption/reaction period. Also included are the estimated values for a hypothetical feed of 20 ppm TCE using the same desorption/reaction conditions as for Run 55 but with the adsorption period lengthened. From this table, it is seen that the potential for energy savings over conventional technology increases significantly as CVOC feed concentration decreases. Since CVOC concentrations of 20 ppm or less are often found in pump-and-treat remediation situations, this technology should be especially suitable for such applications.

6. Conclusions

- The dual function media used in this work provided greater than 99% destruction of TCE when operated in the sorbent/reaction mode.
- The specific bed heating parameters used during desorption/reaction significantly affect the percentage conversion and the desorption/reaction time for the system.
- Based on the estimated savings in sensible heat duty for the process, the process appears most applicable at lower TCE feed concentrations (<100 ppm).
- The significant energy savings (~80% to 90%) are believed sufficient to justify further development of this process.

Acknowledgements

Partial funding for this research was obtained from the Strategic Environmental Research and Development Program [SERDP], the US Environmental Protection Agency, and the US Air Force and is acknowledged with appreciation. The zeolite samples were obtained from UOP. Thomas Quick (The University of Akron) collected the x-ray diffraction data. The contents of this paper should not be construed to represent US EPA Policy.

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