LA-UR -92-1312

Conf

-4

LA-UR--92-1312

DE92 013534

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

TITLE PACKED BED REACTOR TREATMENT OF LIQUID HAZARDOUS AND MIXED WASTES

AUTHOR(S) Roger A. Tennant, CLS-2; Paul J. Wantuck, CLS-2; Rudy Vargas, CLS-2

SUBMITTED TO Spectrum '92 Nuclear and Hazardous Waste Management International Topical Meeting, Boise, Idaho, August 23-27, 1992

DISCLAIMER

Los Alamos Los Alamos National Laboratory
Los Alamos, New Mexico 87545

PACKED BED REACTOR TREATMENT OF LIQUID HAZARDOUS AND MIXED WASTES

Roger A. Tennant, Paul J. Wantuck, and Rudy Vargas
Chemical and Laser Sciences Division
Los Alamos National Laboratory
Los Alamos, NM 87545
(505) 667-4686

ABSTRACT

We are developing thermal-based packed bed reactor (PBR) technology as an alternative to incineration for treatment of hazardous organic liquid wastes. The waste streams targeted by this technology are machining fluids contaminated with chlorocarbons and/or chlorofluorocarbons and low levels of plutonium or tritium. The PBR offers several distinct advantages including simplistic design, rugged construction, ambient pressure processing, economical operation, as well as ease of scalability and maintainability. In this paper, we provide a description of the apparatus as well as test results using prepared mixtures of machining oils/emulsions with trichloroethylene (TCE), carbon tetrachloride (CCl_4), trichloroethane (TCA), and Freon TF. The current treatment system is configured as a two stage device with the PBR (1st stage) coupled to a silent discharge plasma (SDP) cell[1,2]. The SDP serves as a second stage for further treatment of the gaseous effluent from the PBR. One of the primary advantages of this two stage system is that its suitability for closed loop operation where radioactive components are well contained and even CO_2 is not released to the environment.

INTRODUCTION

The DOE complex has a large volume of liquid wastes that need to be treated and disposed of in a manner consistent with environmental, safety, and health (ES&H) laws and regulations. Some of the current and proposed treatment processes are not acceptable to the American public; hence finding other, preferably closed loop, alternatives is desirable. Los Alamos National Laboratory is developing technology that represents a potential improvement over many of the techniques currently used for destruction of hazardous compounds. One of the processes under development relies upon packed bed reactor technology to safely react many hazardous, characteristic, and mixed wastes into more acceptable compounds without adding other potentially hazardous materials to the environment.

The primary motivation for our current effort is the need to construct innovative treatment apparatus to process the large volume of predominantly chlorocarbon contaminated machining oils and emulsions presently stored at the Rocky Flats facility. These fluid wastes, generated during the preparation of nuclear materials, are also contaminated with low levels of plutonium.

Thermal PBR technology offers several distinct advantages for the treatment of such liquid waste. First, the PBR operates near ambient pressure and below normal flammability limits. It also relies upon an external energy source to initiate and control the

chemical reactions occurring in the bed material. Hence, the unit qualifies as a thermal treatment unit. Second, because the PBR technology is relatively simple and rugged, the initial startup costs are low, the system is inherently scalable, and the apparatus survivability and ease of maintainability should be extremely high. Third, when treating oil-based compounds, the bed (once initiated) utilizes the energy content of the fluid to sustain operation. Finally, the physical size of a PBR as well as its low pressure operation make it an attractive candidate for incorporation in a glove box to process radionuclide contaminated waste streams.

DESCRIPTION OF APPARATUS

A diagram of the treatment system with the PBR first stage is shown in Fig. 1. The thermal PBR consists of the following major parts: main reactor enclosure (cylindrical metal pipe), bed material, and an electric furnace. As currently designed, the bed reactor is a stainless steel tube with a diameter of 6.35 cm and a length of 106.7 cm. Historically, for applications like stack gas purification,[3] hydrocarbon cracking processes,[4] and hazardous waste gas treatment,[5] PBR systems have utilized a large variety of bed materials and hence relied upon different reaction mechanisms. For our essentially, non-catalytic process, alumina appears to be a good choice for a bed material. Other materials, such as calcium carbonate, can be added to the bed to enhance the removal of certain produce compounds (such as HCl).

The initial heat source for the reactor is an external, single zone electric tube furnace. An operating temperature between 500 to 1300 C is generally required depending upon the composition of the fluid to be treated. During actual operation, the energy content of the fluid reduces or eliminates the need for continuous application of external energy to sustain chemical reactions in the bed.

The liquid waste is atomized above the bed using a simple coaxial, oxidizer-gas-assisted nozzle. The liquid essentially gasifies in its passage through the bed, and reacts with both the oxidant and oil thermal decomposition products (such as H atoms) producing easily handled materials at the bed exit. Such reaction products include the expected CO_2, H_2O, and HCl as the major exhaust constituents as well as trace quantities of CO, CH_4, and the remaining solvent. Upon exiting the bed, the gas is then cooled down using a heat exchanger, analyzed as to its composition, and either sent to the second stage SDP for further processing or exhausted through a filtered stack.

RESULTS

Tests have been conducted with chlorocarbon, chlorofluorocarbon, and hydrocarbon compounds in the bed reactor with oxidizer gas flow rates of up to 2.5 scfm and organic/aqueous mixtures flow rates as high as 6 gms/min. The primary diagnostic equipment available for analyzing the exhaust stream include an infrared spectrophotometer, a gas chromatograph (GC), and a mass spectrometer. Typically, during steady state operation, the chlorocarbon solvents are removed by the PBR alone to the less than 1 ppm level. Figure 2 shows a typical gas chromatogram trace for a representative TCE test after treatment by the PBR. The influent stream in this case was 5% TCE (by volume) in oil. Analysis of the effluent stream shows that the initial TCE concentration has been reduced to the 0.1 ppm level. During startup and shutdown, transient behavior in the PBR does allow larger concentrations of chlorocarbons and reaction products to remain in the effluent stream. Figure 3 shows a time history of the GC-measured TCE concentration present in the effluent. During the first 15 to 20 minutes, TCE concentrations of up to 80 ppm were observed along with methane at a 17 ppm level.

During upset conditions and shutdown, the methane level rose to a 5-10 ppm level. The second stage SDP processes the PBR effluent very effectively and thus will easily handle startup and shutdown transients. The effluent concentrations of other solvent materials treated in the PBR are presented in Table I.

Table I. Chlorocarbon and Chlorofluorocarbon Solvents Tested in the PBR

Liquid	Influent Concentration	Effluent Concentration
TCE	up to 10% (in oil)	0.1 ppm
CCl_4	3% (in oil)	<1.0 ppm
TCA	up to 10% (in oil)	<50ppm
Freon TF	up to 20% (in oil)	<50ppm

OTHER TECHNICAL ISSUES

At this juncture, the thermal PBR represents a laboratory size device. Other key issues that need to be addressed for a prototype system include, scalability, corrosion resistance, thermal management including radial temperature uniformity, how to safely process radioactive contaminated waste, and the ability to reduce chlorocarbon/hydrocarbon concentrations to sufficiently low levels for discharge to the air.

Scalability of a PBR is a very important consideration, but there are no obvious limitations on size or anticipated performance. The current data is obtained using a reactor that is only 6.4 cm in diameter. A 15.2 cm reactor, currently under fabrication, will allow a study of gas and liquid chemical conversion processes at gas flow rates up to 25 scfm and liquid injection rates as high as 100 gms/min (about 1.6 gal/hr). Based on current data from th 6.4 cm OD reactor, a system designed for operation in the 100 to 200 scfm regime would require a bed with a diameter of between 30.5 to 45.7 cm and a length of approximately 1.2 m. The tube furnace could be constructed to ceramic heater elements commonly used in industry. Such heater elements are available in diameters ranging from 0.75 to 39 inches. The startup electrical power requirement for a 30.5 to 45.7 cm unit would be about 15 to 20 kW.

When decomposing chlorocarbons, HCl is formed. Since water is also formed as a reaction product, the resulting mixture is quite corrosive even at low concentrations. To eliminate extensive corrosion problems, the simplest technique is to react away the HCl in the bed itself. This could be done by using a material such as limestone in the last 12 to 18 inches of the reactor bed. The chloride reaction product would be calcium chloride which would stay in the bed. Another approach is to allow the HCl to pass out of the bed and to be collected by a water scrubber downstream and hence be disposed of as an acid waste. In addition, the use of readily available materials like Haynes alloy pipe for bed reactor container construction effectively minimizes such operational difficulties as acid corrosion, high temperature, and the oxidizing environment. For an even longer operating life, a ceramic vessel could be used.

Thermal management and temperature distribution in a packed bed reactor are important considerations. Chemical reaction of organic compounds contribute to the heating of the bed thereby reducing or in some cases eliminating the electrical power requirement. These chemical reactions and the released heat help to drive other chemical reactions to completion (thereby forming carbon dioxide, water vapor, and salts).

The ability to generate a uniform radial temperature distribution may limit the maximum size of the PBR. The ability to generate a uniform radial temperature distribution

will depend both on the amount and the properties of the fluid to be treated. Tests on the 15.2 cm PBR will further define actual requirements.

Under some circumstances, additional treatment systems and/or closed loop operation may be desirable (see Fig. 1). A typical circumstance would be if an acceptable level of removal of some compound is not achieved (such as observed during start up transients). Additional stages could be a silent discharge plasma system, a water scrubber for acid gas removal, a water condenser, a carbon dioxide to carbonate conversion device, or another bed reactor stage. Part of the research effort will be to determine through detailed on-line chemical analysis of the packed bed effluent whether additional stages are necessary and if so what they should be.

SUMMARY

The Chemistry and Laser Sciences Division (CLS) at Los Alamos National Laboratory has developed a PBR technology that can safely react many hazardous, characteristic, and mixed wastes into more acceptable compounds without adding other potentially hazardous materials to the environment. The chlorocarbon solvent concentration in the effluent has been measured at the <1ppm level.

We have extended PBR operation into a high temperature regime (up to 1300 deg C). The high temperature capability of our PBR appears to have eliminated saturation and tar accumulation problems. The chosen void fraction of the bed has minimized the effect of miscellaneous residues. The bed reactor operates at local atmospheric pressure; hence, the reactor is not a pressure vessel. Therefore, an extensive high temperature pressure vessel certification program shouldn't be necessary and the PBR represents a very suitable technology for glovebox incorporation for mixed waste treatment.

The current scale of test reactors has demonstrated feasibility for larger sizes. Scaleup efforts in progress will provide the necessary data for the design of such systems. Key issues being addressed include scalability, survivability and maintainability, handling of the acid gas reaction products, corrosion resistance, thermal management, bed temperature uniformity requirements, and the capability to reduce the chlorocarbon/hydrocarbon concentrations for direct discharge to the air.

ACKNOWLEDGEMENT

This work was performed under the auspices of the Department of Energy.

REFERENCES

1. J. J. COOGAN, G. K. ANDERSON, H. G. HECK, M. KANG, W. H. McCULLA, L. A. ROSOCHA, R. A. TENNANT, and P. J. WANTUCK, "Advanced Combustion and Oxidation Techniques for the Destruction of Hazardous Wastes," Paper to be presented at SPECTRUM '92, August 23-27, 1992, Boise, Idaho.

2. W. H. McCULLA, L. A. ROSOCHA, W. C. NEELY, E. J. CLOTHIAUX, M. M. KUSHNER, and M. J. ROOD, "Treatment of Hazardous Organic Wastes Using Wet Air Plasma Oxidation," First INEL Plasma Applications to Waste Treatment Workshop, Idaho Falls, Idaho, January 16-17, 1991.

3. J. D. DALTON, R. L. GILLINS, T. L. HARRIS, AND H. L. WOLLERMAN, An Assessment of Offgas Treatment Technologies for Application to Thermal Waste

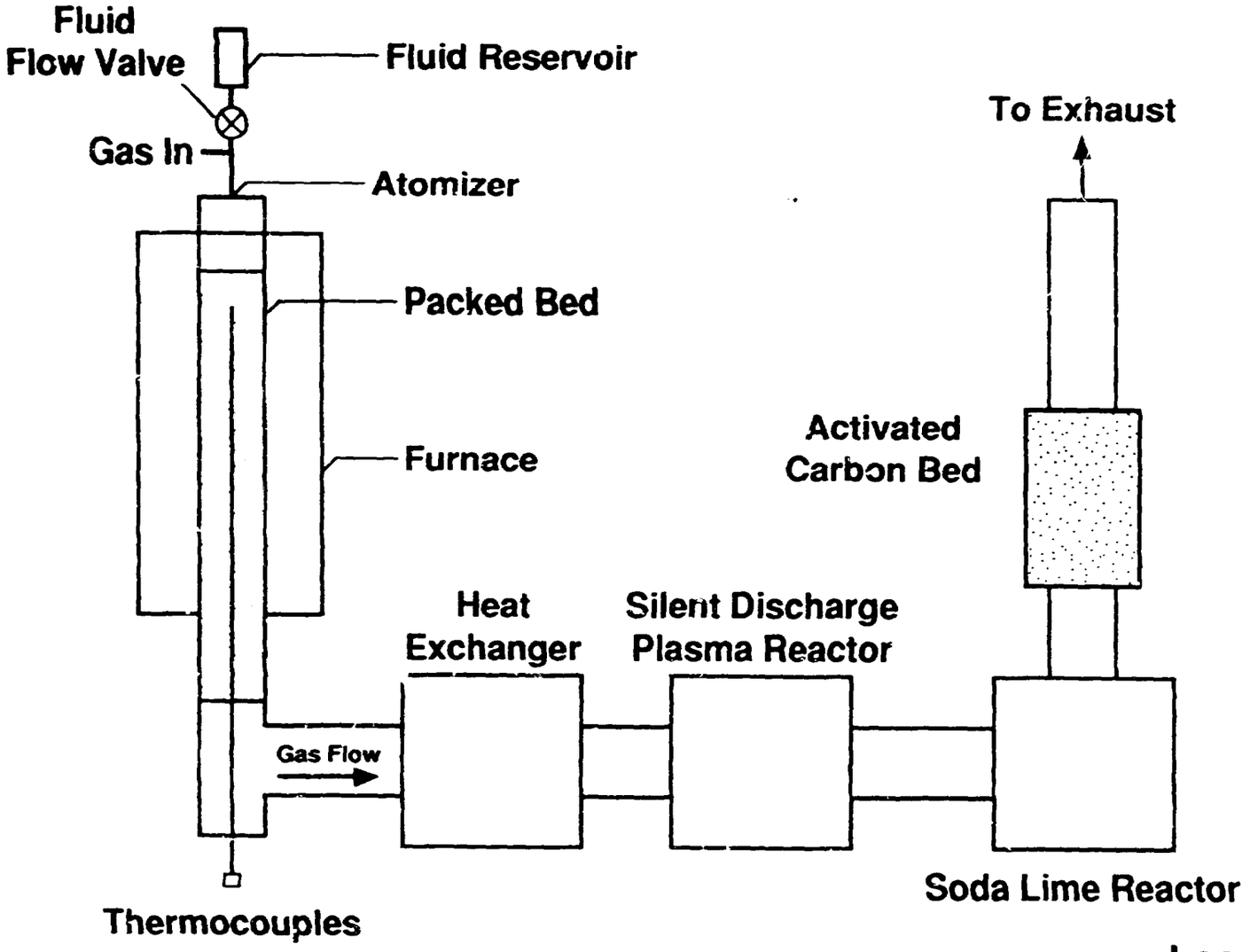
Treatment of Department of Energy Wastes, SAI Corporation Report, Idaho Falls, Idaho, (1991).

4. G. DJELVEH, J. B. GROS, AND R. BUGAREL, "Simulation of a Catalytic Packed Bed Reactor in the Oxidation of Propene," Can. J. of Chem. Eng., Vol. 60, pp 146-152 (1980).

5. P. J. MAWLE AND J. R. SMITH, "Converting to Solids," European Semiconductor, November 1989.

Figure 1

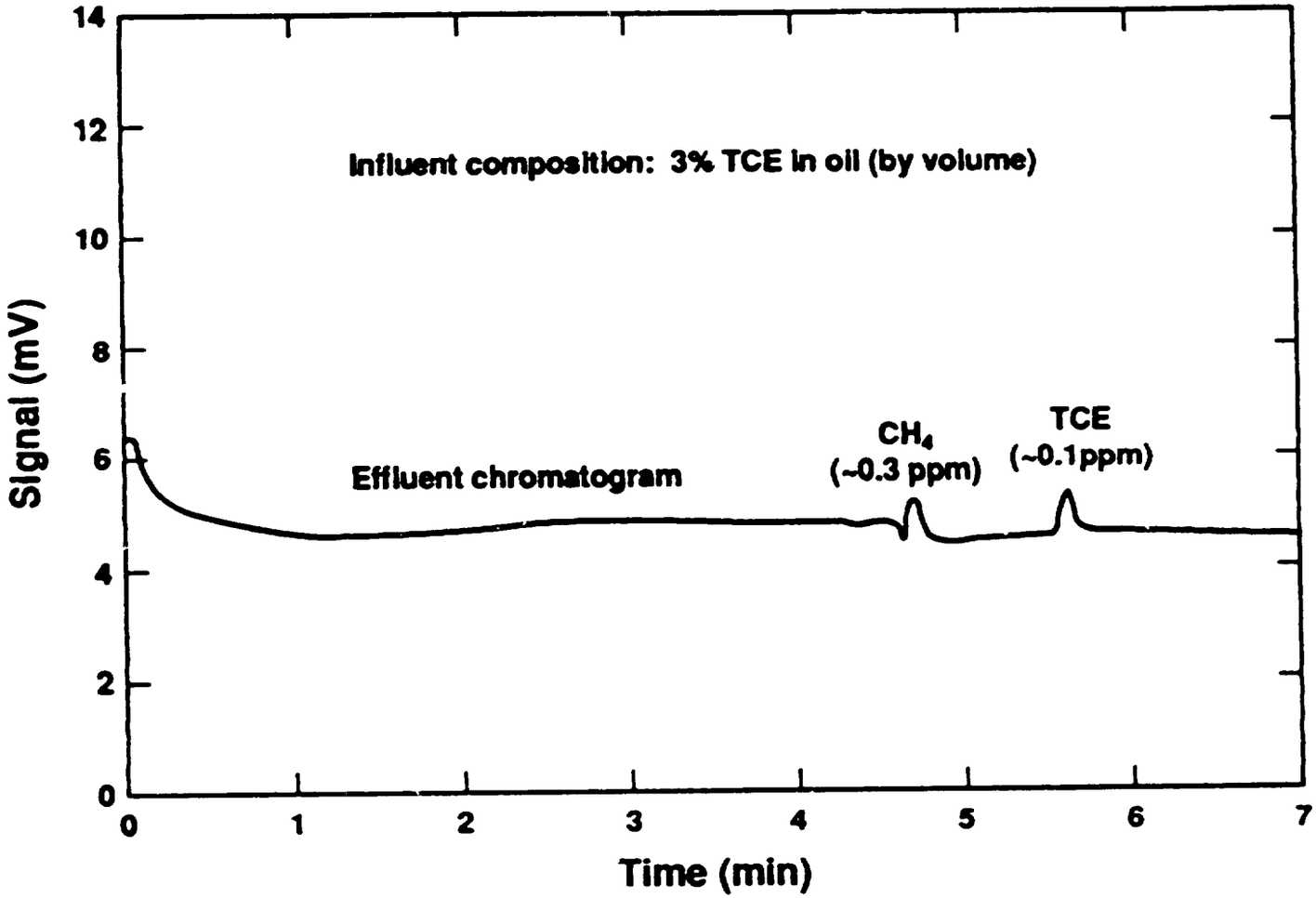
Packed Bed Reactor - Silent Discharge Plasma System



Los Alamos

CLS-91-2471

Fig. 1. Packed Bed Reactor / Silent Discharge Plasma Treatment System



Los Alamos
CLS-92-513

~~Figure 2~~

Fig. 2. Effluent Gas Chromatogram for 3% TCE in oil Influent stream composed o

Figure 3

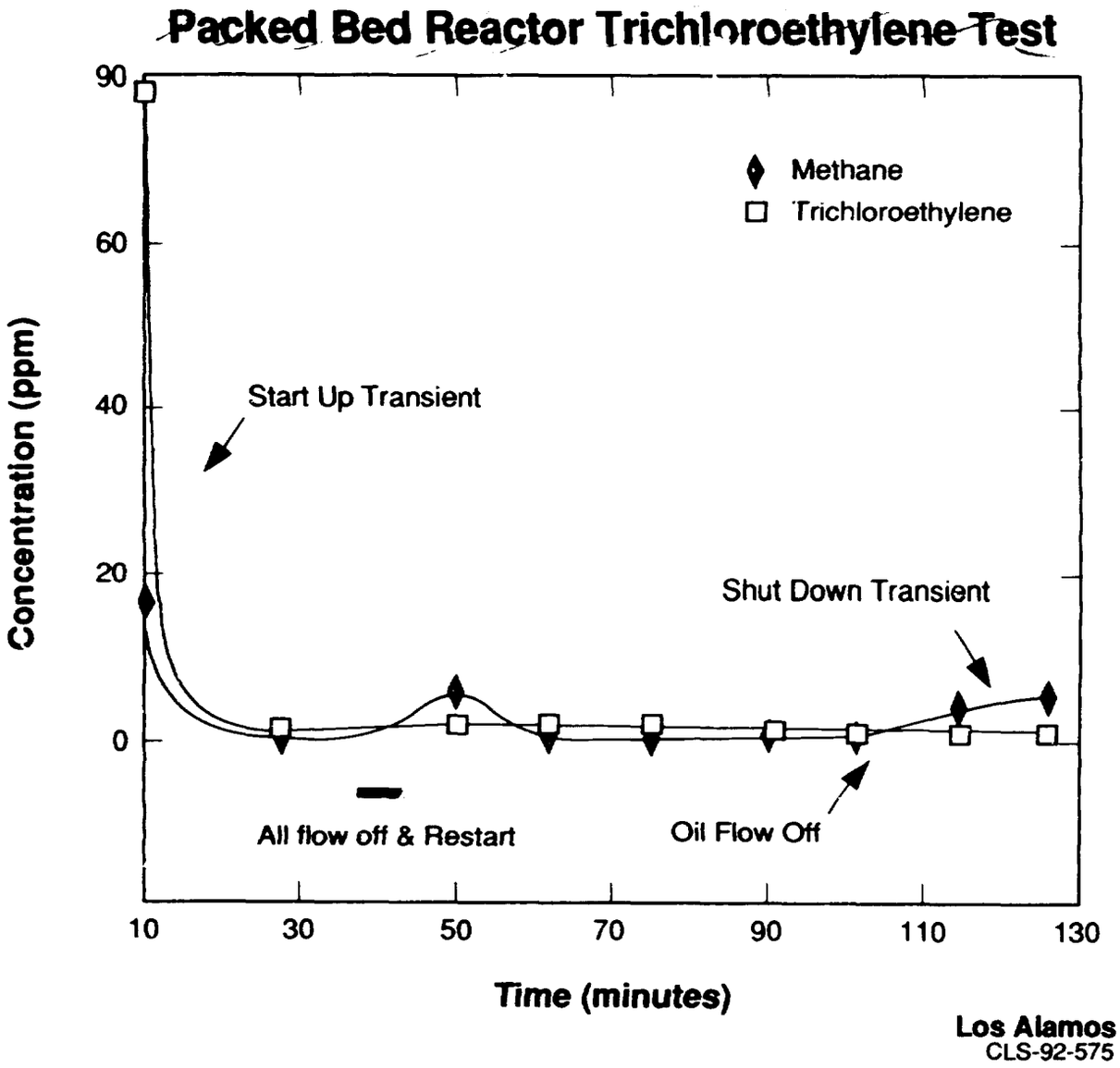


Fig. 3. Effluent Composition as a Function of PBR Run Time; Influent = 3% TCE in machining oil