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URANIUM EFFLUENT TESTING FOR THE OAK RIDGE TOXIC SUBSTANCES CONTROL ACT MIXED WASTE INCINERATOR

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INTRODUCTION

The Oak Ridge K-25 Site Toxic Substances Control Act (TSCA) Incinerator has been undergoing a series of routine tests to determine uranium partitioning to the stack, scrubber waters, and bottom ash. This paper discusses the results of the most recent experiment, in which relatively high rates of uranium stack gas emissions were identified: 6.11g/h or 8 wt % based on the uranium feed. These data are compared with earlier data, and an empirical correlation is suggested between the stack emissions of uranium and the product of the uranium and chlorine concentration of the feed. This is consistent with certain findings with other metals, in which increasing chlorine feed contents led to increasing emissions.

TEST RESULTS AND CONCLUSIONS

Table 1 provides a summary of the principal test results. The particulate emissions rate of 0.025 grains/dry std ft^3 was within the regulatory limits of 0.08 max grains/dry std ft^3. The Environmental Protection Agency (EPA) Method-5 sampling train and fluorometric analysis for uranium were used. Median particle diameter in the quench blowdown was 0.37 μm and 0.31 μm in the ionizing wet scrubber (IWS) liquors.

Table 1. Summary of major test results

		Percent of feed
Uranium stack gas emissions	6.11 g/h	8
Particulate stack gas emissions	0.025 grains/dry std ft^3, 7% O_2	23 (basis feed ash content)
Median particle diameter in scrubber liquors	Quench: 0.37 μm IWS: 0.31 μm	
	Uranium distribution	
Quench blowdown	29 g/h	38 (basis feed uranium)
IWS blowdown	19 g/h	25 (basis feed uranium)

TEST PROGRAM SUMMARY

The emissions test was conducted like two earlier experiments.[1,2] However, on December 11, 1991, only one run was made, and fewer data were collected.

The incinerator feeds were as follows:

- waste oil from the Oak Ridge Y-12 Plant and the Paducah Gaseous Diffusion Plant and
- aqueous phase from the tanker rinse of this same oil.

Test Program

The incinerator was operated at the appropriate TSCA conditions. The organic feed to the secondary combustion chamber SCC was delivered at a very steady rate of ~400 lb/h. It contained the bulk of the ash (1.8 wt %). The aqueous feed rate was less steady but averaged ~300 lb/h to the primary combustion chamber PCC (kiln). If the uranium fed to the incinerator, ~21% was fed to the kiln, and 79% was fed to the SCC (on-line analysis basis). This feed arrangement provides a worst-case scenario for the entrainment of stack particulates because the off-gases from the SCC do not pass through the mix chamber, where ash particles may drop out.

Samples of the feed material were taken from the holding tanks before the run and from the flowing feed streams approximately every 30 min during the experiment. The results of the analyses for the composites of the flowing stream and the prerun samples are shown in Table 2. Samples of scrubber liquors from the points shown in Fig. 1 were also taken every 30 min. The recycle solutions represent (1) a commingling of the quench and venturi scrubber liquors, henceforth called the quench, and (2) a commingling of the packed bed and IWS liquors, henceforth called the IWS purge. Composites of the samples from each stream were made and the uranium partitioning determined from the flow rates and concentrations.

Stack samples were taken isokinetically according to EPA Reference Method 5 at the second (upper) sampling level of the stack. Separate trains and probes were used to collect uranium and particulates. A. Andersen, Inc., brand stack samplers were used.

The waste-burner flame was blue-white and of good quality throughout the test. The aqueous waste lance flow pulsated, owing to the characteristics of the pump.

Table 2. Feed analyses

	Tank 307A (aqueous feed) - 031		Tank 305B (organic feed) - 031	
	Prerun analysis	On-line analysis	Prerun analysis	On-line analysis
Uranium, ppm	229	118[a, b]	0.398[c]	336[a]
Heat content, Btu/lb	<50		11,300	
Phosphorous, ppm	2500		7510	
Sulfur, ppm	<500		4753	
PCB[d] content, ppm	4.1		3000	
Chlorine, ppm	<500		10.475% (organic)	
Ash, %	0.10		1.81	
Density, g/cm^3	0.98		0.960	
Viscosity, centipoise	4.81		63.5	
Uranium, μCi/g	3.42E-3		1.83E-4	

[a]Weighted averaged of four measurements, two samples.
[b]Large spread in data.
[c]Suspicious point.
[d]Polychlorinated biphenyl.

Deviations from the Plan and Normal Operations

Forty minutes elapsed between the time the feed was first introduced to the incinerator and the time samples were first taken. Though this was unintentional, it afforded an opportunity for the incinerator scrubber streams to approach a steady state. The first sample of aqueous feed was taken from a point near the incinerator, rather than from a point near the pump discharge, because of a plugged line. The "hot box filter" of the stack particulate sampling train exceeded its regulatory-allowed maximum temperature value of 273°F by 7° for several minutes. This could result in a slightly greater amount of material volatilizing during this time if the materials' vapor pressure were affected by the 7° temperature excursion. This phenomenon is unlikely to affect uranium partitioning data, however. The IWS #1 unit began its wash cycle 3 h into the run and operated for 6 min. In determining the velocity profile, only five of the desired stack traverses were completed along the second diameter, perpendicular to the first. All seven along the first diameter were completed and allowed an extrapolation of results. However, this difficulty would invalidate the test in terms of regulatory compliance.

RESULTS AND DISCUSSION

Sampling and Analysis

The flowing-stream samples and the prerun uranium analyses are quite different, as is not uncommon in these tests. Because stratification in large tanks exists even with maximum available agitation, the flowing-stream samples are chosen to be the basis of all mass balances, as in earlier tests. The analytical agreement between prerun sample and flowing-stream samples for uranium was reasonable in the aqueous feed. In the organic feed, however, the prerun uranium analysis and that of the flowing-stream samples differed by a factor of nearly three orders of magnitude. The two organic-feed, flowing-stream samples were analyzed in duplicate for uranium, and all the results were reasonably repeatable, providing confidence in their accuracy, while the prerun result was based on one sample and one analysis. The flowing-stream sample analysis was therefore used for mass balance calculations.

Organic samples were agitated and small aliquots removed for oxidation in a Parr Bomb, and results were fairly reproducible, as noted. The aqueous samples, however, were less homogeneous and contained some small globules of organic material. Evaporation of the aqueous phases in a furnace preparation technique—Martin Marietta Energy Systems Analytical Chemistry Division (procedure ACD-192807.R1)—using a larger aliquot than the Parr Bomb technique would accept, appeared to be more suitable for these samples. Because the aqueous samples were so heterogeneous, a larger aliquot allowed a more representative sample to be prepared. This preparation technique is suggested for future aqueous samples containing small amounts of organics.

Feed

The amount of uranium fed during this experiment, based on flowing-stream samples, was 77 g/h (similar to past experiments), as shown in Table 4. Total phosphorous was 1200 g/h, a higher rate than in January 1991[1] and lower than that in August 1990,[2] when the uranium was held fairly insolubly in the ash. Uranium and other elements were in moderately high concentrations in the organic feed in this test, as has been found in previous high-ash feeds to the incinerator.

Air Emissions

The particulate emissions rate of 0.025 grain/dry std ft^3 of stack gas (corrected to 7% oxygen) is extremely close to the 0.0249 grain/dry std ft^3 average result from the 1989 RCRA trial burn, in which a combination of liquids and solids was incinerated.

The uranium stack result was 6.11 g/h, which is greater than the 3 g/h recorded during August 1990.[2] The pH of the IWS recycle solution, particularly of IWS #2 (according to R. W. Anderson), may be important in explaining this result. At high pH, carbon dioxide is absorbed, thus enhancing uranium solubility as a uranyl carborate, though substance has not been identified as yet. If mist entrainment does occur, it could result in higher stack emissions. The IWS operated at a pH of approximately 8 during the test, although it reached the undesirable maximum of 10 several times.

The feed concentration of organic chlorine in this test was ~10 wt %, much higher than in previous tests.

Evidence in the literature on coal combustion and incineration supports the hypothesis that metals or metal compounds that are volatilized will preferentially form fine fume or enrich the surface of the finer particles.[3] Although other mechanisms are not rejected, this mechanism is gaining acceptance. Many metal chlorides are relatively volatile; the EPA has found correlations between emissions of lead Pb, cadmium, and other metals that can form stable chlorides.[4] Fine particles in the range between 0.1 and 1 μm pose the most challenging scrubbing problems and might be expected to reach the final scrubber stages and the stack.

Emissions and feed data are shown in Table 3 for three experiments with uranium conducted to date. The uranium emissions are plotted in Fig. 2 with respect to the product of the uranium and chlorine content in the feed. The abscissa is in relative units of concentration, and the ordinate represents uranium stack gas emissions in grams per hour. The stack gas flow rate was slightly higher in 1990; however, no correction was made for it. A correlation coefficient of 0.921 exists in this plot. If the uranium emissions are plotted against the chloride content of the feed alone, the correlation coefficient R is 0.85.

The formation of the volatile UCl_4 (bp = 789° C) is offered as a possible explanation of these results. It is well known that UCl_4 can form from the reaction of UO_2 and CCl_4 in the absence of moisture. The incinerator feeds, while not containing CCl_4, contained, in the case of the December 1991 experiment, large quantities of highly chlorinated organics similar to CCl^4. Whether or not the UCl^4 could form in the secondary combustion chamber at 1200° C in the presence of varying amounts of water is a question to be further examined in laboratory-scale experiments.

Table 3. Comparison of uranium and chlorine feeds with stack emissions

Test dates	Uranium in stack gas (g/h)	Uranium in stack gas (% of fee)	Uranium in feed (g/h) PCC	SCC	Total	Chlorine in feed (g/h)
8/27/90	2.83	2.9	96.6	0	96.6	2,400
1/18/91	0.136	0.39	24.8	9.9	34.7	3,755
12/11/91	6.11	7.94	16.3	60.7	77.0	19,000

Aqueous Emissions

The uranium and total-dissolved-solids (TDS) concentrations in the quench recycle and IWS recycle are shown in Table 4. The partition coefficients of uranium are also shown for comparison with data from previous emissions tests.

The TDS were determined on the two purge streams in an attempt to correlate the results with the stack particulate emissions. If mist entrainment were occurring from the IWS #2, dissolved solids could collect in the stack gas particulate sampling train. The TDS concentrations in the IWS/packed-bed recycle in this experiment were lower than those in the 1989 RCRA burn: 1.6 vs 3.4 g/L. The TDS concentration in the quench recycle was much lower in this experiment than that in the RCRA burn: 3.4 vs 55 g/L. The RCRA burn included 260 lb/h of chlorine HCl, a much higher value than for the December 1991 test, and this could logically have resulted in the higher TDS in the former test.

Scrubber Liquor Particulates

Particle size data were obtained on quench and IWS recycle streams to assess the scrubber performance. Electron micrographs were made of the specially centrifuged and washed solids from the purge samples. The micrographs were then subjected to Kevex image analysis, in which the cross-sectional area of the particles is measured and a tabulation of their equivalent diameter size distribution is produced, assuming that the particles are spherical. In the case of the solids, this was a good assumption, as was confirmed by scanning electron micrography. This spherical morphology, commonly seen in fly ash, suggests that, for a time during combustion, the ash was in molten form. The median Waddel diameters for the particles (number-basis distributions) are 0.31 μm for the IWS recycle stream (Fig. 3) and 0.37 μm for the quench recycle stream (Fig. 4); the computed lognormal particle size distributions for these materials are presented in Fig. 5. These particle sizes are similar but are much smaller than the median values of 0.75 μm (IWS) and 1.2 μm (quench) recorded for testing on January 18, 1991,[1] using the same analytical methodology.

Elemental analysis was quantitatively measured by energy dispersive X-ray spectroscopy. It revealed the presence of titanium much more prominently than in past experiments. Titanium is a very refractory metal, except in its chloride forms. Its penetration to the IWS may be consistent with the volatilization condensation particulate formation mechanism and the high chlorine feed. The prominence of titanium could also be a result of very slightly higher feed concentrations of titanium (4 ppm in this run vs ~1 ppm in past runs) and consequently entrainment and have of no special significance.

Table 4. Results of aqueous scrubber emissions

	Uranium concentrations (ppm)	Total dissolved solids (g/L)	Uranium partitioning (%)			
Test dates	12/11/91	12/11/91	12/11/91	1/18/91	1/16/91	08/27/90
Quench	4.9	3.5	38	29.7	35.5	1.4
IWS	4.1	1.5	25[a]			

[a]Limited data.

CONCLUSIONS AND RECOMMENDATIONS

It appears from the data on particulate and uranium emissions that the IWS is performing within specification regarding stack particulates. The relatively high uranium stack emissions could possibly result from the combination of the feeding of the organic waste entirely to the SCC and the high organic chlorine concentration. A chemical analysis of the stack particulate emissions could confirm or deny the uranium chloride volatilization process hypothesis, provided similar feeds and conditions were used. Lessons were learned regarding sample collection and analysis that should benefit future emissions experiments, and the data base has been advanced as a result of this project. These results suggest that the emissions are not improved when wastes with high chlorine and uranium content are fed to the SCC.

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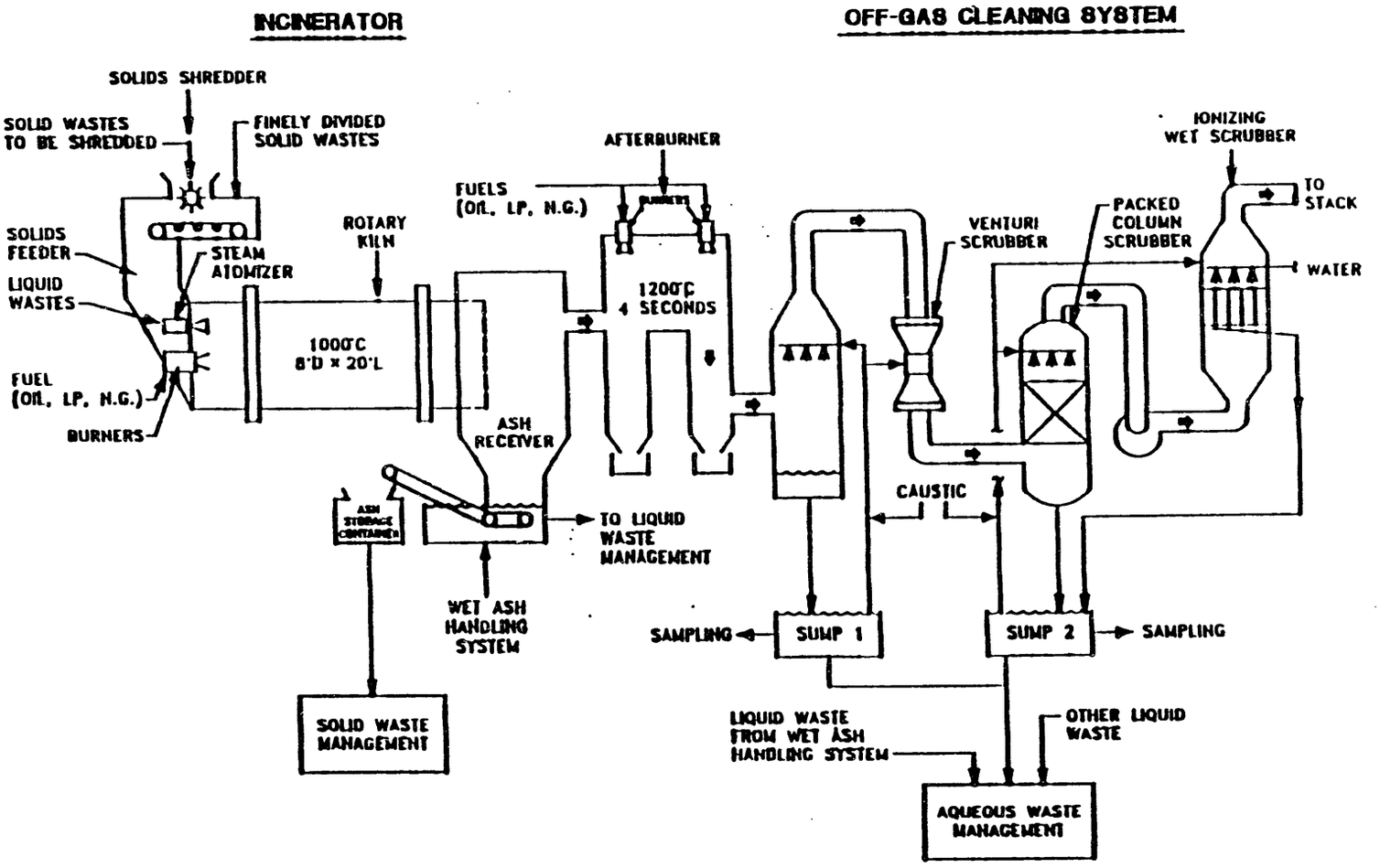

Fig. 1. Incinerator and liquid sampling locations.

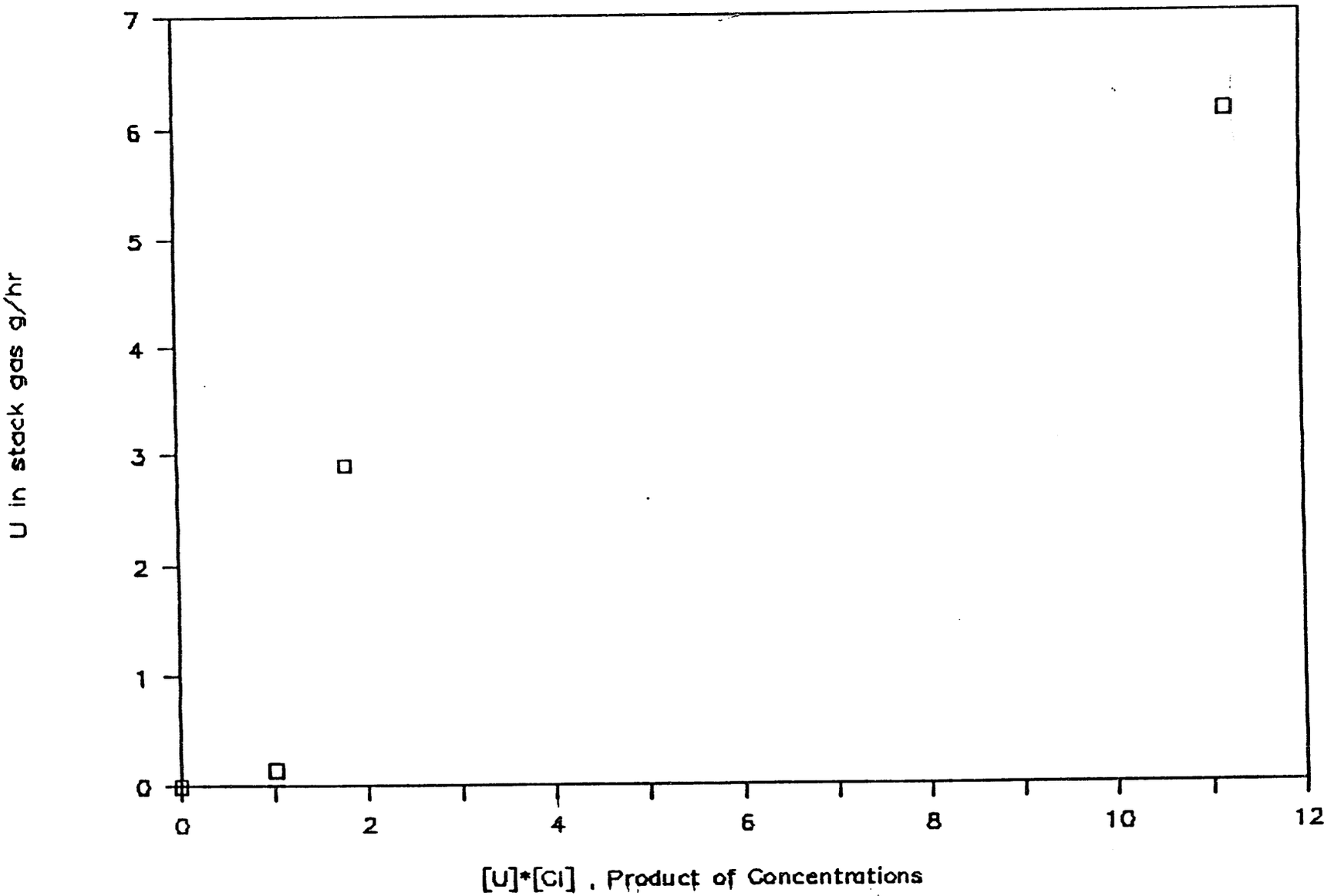

Fig. 2. U Emissions vs. Relative Concentration

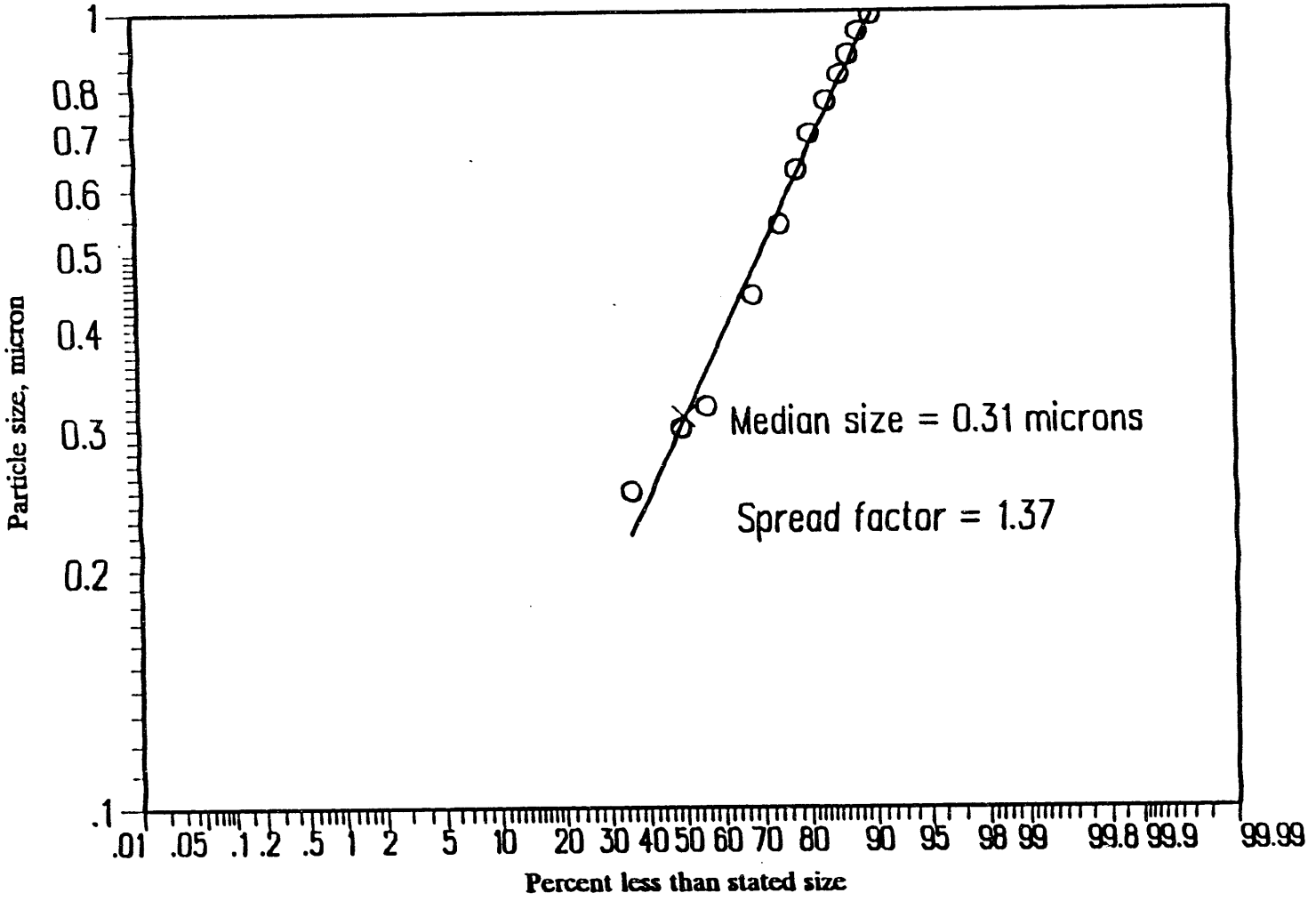

Fig. 3. Lognormal probability plot of particle size in sample from IWS on December 11, 1991.

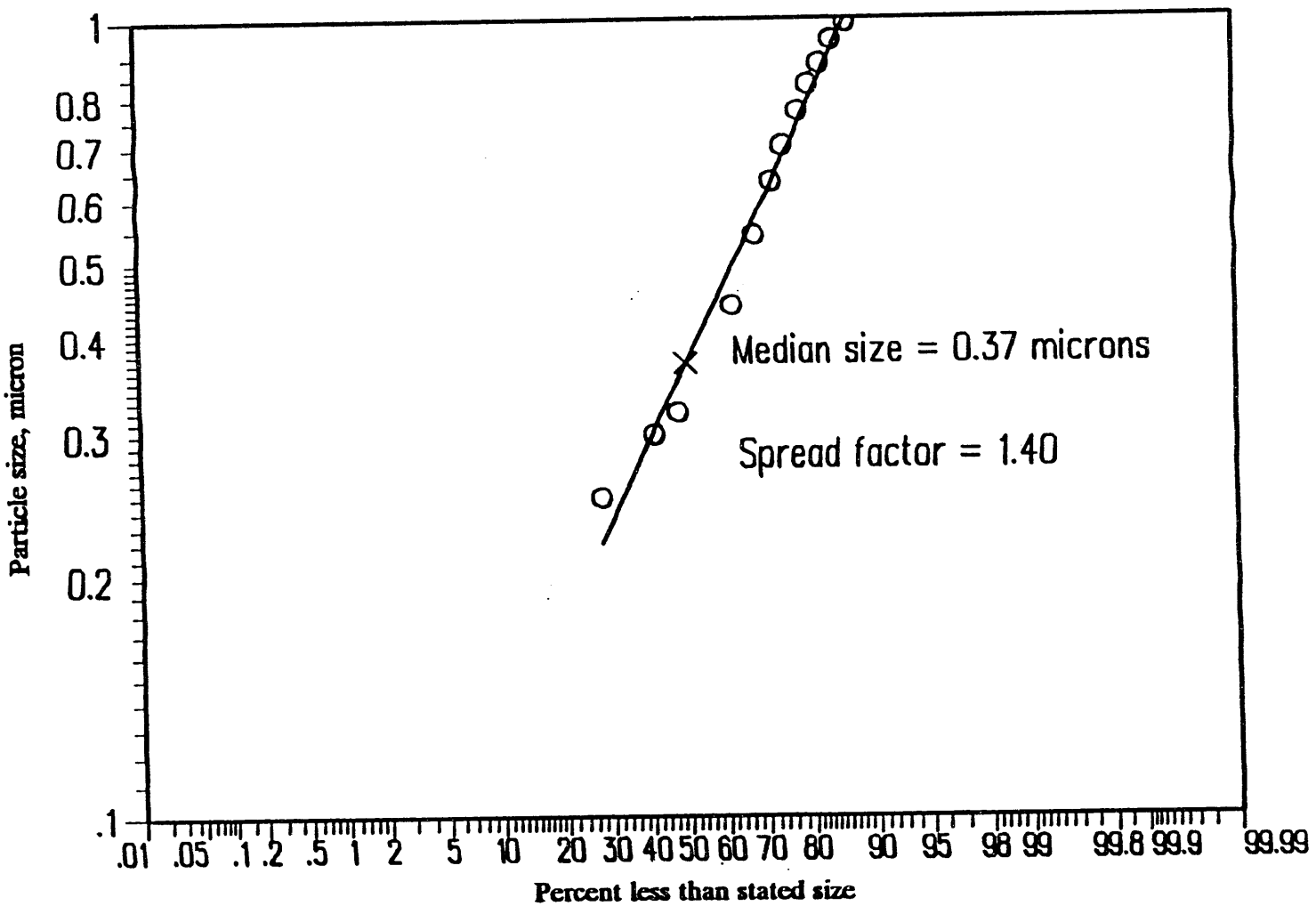

Fig. 4. Lognormal probability plot of particle size in sample from quench on December 11, 1991.

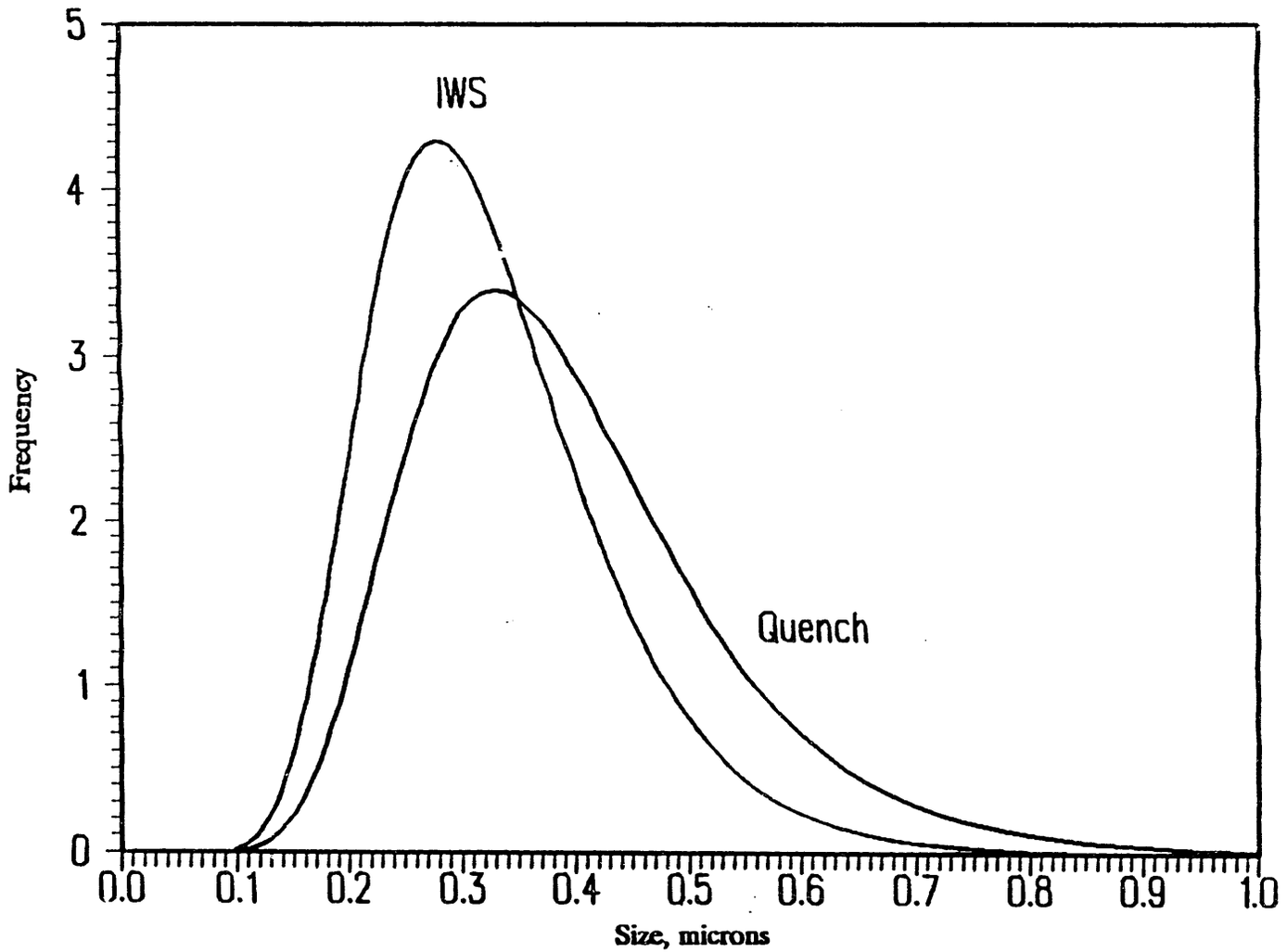

Fig. 5. Lognormal particle size distribution samples of December 11, 1991.

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