The Effects of Size Reduction Techniques on TCLP Analysis of Solidified Mixed Waste

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Introduction:

The Rocky Flats Plant (RFP) generates and stores mixed wastes that are subject to regulation under the Resource Conservation and Recovery Act (RCRA) Land Disposal Restrictions (LDR). Low level mixed wastes at RFP are destined for disposal at the Nevada Test Site (NTS), and thus must meet stringent NTS Waste Acceptance Criteria (WAC), including free liquids, dispersible solids, and Toxicity Characteristic Leaching Procedure (TCLP) requirements.

TCLP requires size reduction of the waste form to less than 0.95 centimeters. This can be accomplished by cutting, crushing, or grinding. These classic size reduction methods have the effect of exposing more surface area of the waste.

One of the stabilization technologies under investigation at RFP is polymer encapsulation by co-extruding the waste with low density polyethylene. This results in a monolithic waste form that is mechanically superior to, and less permeable than, some other processes typically used in industry. Another major advantage of the polyethylene extrusion process is that it is a physical, not a chemical, encapsulation process; therefore, the process is insensitive to chemical variations in the waste stream. A drawback to the physical encapsulation of the waste is that dissolution of the waste and migration of the hazardous constituents could occur if the matrix is breached. For polyethylene waste forms, several tens of thousands of pounds of force are required to crush the waste form adequately. Clearly, this is an unrealistic size reduction method for polyethylene encapsulated waste forms. When exposed to high pressures, the polyethylene tends to fail along the polyethylene-waste interface. This breaches the physical barrier enclosing the waste and exposes it to the leaching solution. Chemical stabilizers can be added to immobilize hazardous constituents through chemical means. Although breaching of the polymer matrix is highly unlikely under any likely transportation and storage conditions, size reduction and thus potential breaching of the polyethylene matrix is required by TCLP.

Another stabilization technology being investigated at RFP is microwave melting. This technology involves mixing the waste with glass forming materials (diatomaceous earth and borax) and melting this mixture to glass with microwave energy. The system developed at RFP includes an "in-drum" melting cavity designed to isolate the molten waste in the shipping container during processing. The resultant crystalline material offers a leach resistant, stable matrix especially suited for wastes containing hazardous and radioactive contaminants. The high temperatures achieved (approximately 1100°C) may also destroy soluble materials such as nitrates, sulfates, and organics.

The objective of this study is to evaluate the effects of different size reduction methods on TCLP results for polyethylene-encapsulated and microwave melted surrogate waste.

Procedure For Polymer Encapsulation:

All of the samples used in this study were loaded 50% with surrogate sludge consisting of technical grade sodium nitrate contaminated with 500 parts per million (ppm) of cadmium (Cd), chromium (Cr), and nickel (Ni). This surrogate waste was used to evaluate the effects of different size reduction methods, and was not intended to simulate any particular waste stream at RFP. The actual waste streams at RFP are expected to have 10 to 50 times less toxic metals. Samples were prepared in the following forms: 1"X2" pucks (heated molds), 2"X4" pucks (non-heated molds), and 2"X4" chemically modified pucks. For the 1"X2" and 2"X4" pucks the size reduction was performed by cutting. The chemically modified 2"X4" pucks were crushed with a press and broken into pieces.

The 1"X2" pucks were used to study the effect of surface area increase on the leachability of Cd, Cr, and Ni. Three pucks were extracted whole, three pucks were extracted after cutting in half, and three pucks were extracted after cutting in quarters.

Three 2"X4" pucks were extracted whole; one puck was cut into cubes smaller than 3/8" on a side prior to extraction. Three samples of the cubes were extracted so that the leachability of Cd, Cr, and Ni from all cut surfaces could be studied.

The chemically modified pucks were made by adding calcium oxide to the surrogate waste before extrusion. Three size-reduced samples were extracted for each level of calcium oxide added to the surrogate waste (12.5%, 15%, and 17.5%). The chemically modified pucks were then spiked with 500ppm of Cd and Cr.

Results for Polymer Encapsulation:

The results for the 1"X2" pucks showed an increase in Cd, Cr, and Ni levels as the exposed surface area increased (see Table 1). This confirms the hypothesis that classical size reduction techniques will increase the leachability of Cd, Cr, and Ni as the surface area of the sample increases.

The results for the 2"X4" pucks showed less leaching than the 1"X2" pucks (see Table 2). This suggests that the more rapidly cooled surface of the nonheated molds resulted in a product that has polymer predominantly at the surface. The 2"X4" puck that was cut into cubes with all surfaces cleaved showed a significant increase in leachability.

The results for the chemically modified pucks showed the least leaching for Cd and Cr of any of the samples (see Table 3). The modifier must be exposed to the extraction fluid to be effective. Therefore, reducing the polymer encapsulated waste to smaller particles yields better results.

Procedure For Microwave Melter Samples:

The size-reduction study samples for microwave melting were taken from a matrix of samples that had various waste loading percentages, melt temperatures, and quench rates. The waste was spiked with 500 ppm of cadmium, chromium, lead (Pb), nickel, and silver (Ag). Samples were prepared by fracturing the original monolith so that a subsample was obtained that was a vertical cross-section of the original monolith. This subsample was further size-reduced by crushing in a vice to obtain a representative piece of approximately 50 grams. TCLP was performed on the 50 gram pieces. Samples that passed this TCLP test were further size-reduced by crushing in a vice. The resulting particles were sieved through a 9.5 millimeter (mm) and a 1.0 mm sieve. Both fractions (9.5 -1.0 mm and smaller than 1.0 mm) were extracted.

All TCLP extract samples were prepared for analysis by EPA Method 3010. The analyses were performed on a Leeman Labs "Plasmaspec" Inductively Coupled Plasma/Atomic Emission Spectrometer (ICP/AES). The analyses were performed using EPA Method 6010.

Results For Microwave Melting:

Table 4 shows the results of six 50 gram samples chosen from the original matrix. Three of the six samples passed TCLP at this size reduction level, and therefore, were further size-reduced.

The size-reduced fraction that was between 9.5 mm and 1.0 mm resulted in one sample that passed TCLP (see Table 5). Cd is the only element that failed TCLP for the other two samples. The size-reduced fraction that was less than 1.0 mm failed TCLP for Cd for all three samples.

Discussion:

Results for the microwave melting studies indicate that this process, under the appropriate conditions, will yield a product that passes TCLP. However, size reduction must be accomplished with less than 10% of the sample reduced to less than one millimeter particle size.

The results for the polymer solidification studies indicate that size reduction has a larger effect on wastes encapsulated using this process than on wastes processed by the microwave melting process. Unlike microwave melting, the polymer solidification process stabilizes waste solely by physical exclusion from the environment. As sample surface area increases, extractability of RCRA-listed metals increases proportionally. Due to the fact that this study was performed with RCRA-listed metals spiked at 10 to 50 times the expected levels, the effect of size reduction on polymer samples will be less than the results of this study. Sample preparation by pelletizing the waste, and then rapidly cooling the pellets, may overcome this problem. Chemical modification of the waste form is also being considered as a solution.

The authors conclude that, in either case, the size reduction step of TCLP does not fairly represent the performance of these stabilization techniques in the environment.

Table 1. POLYMER SIZE REDUCTION STUDY
1 X 2 HEATED MOLDS

units are in ppm

SAMPLE ID	Cd	Cr	Ni
WHOLE PUCK	0.897	0.072	1.237
HALF PUCK	1.176	0.087	1.380
QUARTER PUCK	1.343	0.097	1.740

Table 2. POLYMER SIZE REDUCTION STUDY
2 X 4 NON-HEATED MOLDS

units are in ppm

SAMPLE ID	Cd	Cr	Ni
PUCKS	0.238	0.235	0.312
CUBES	1.083	0.373	1.507

Table 3. CHEMICAL MODIFICATION OF POLYMER SAMPLES

units are in ppm

SAMPLE ID	Cd	Cr
12.5% CaO	0.175	0.800
15.0% CaO	0.098	0.085
17.5% CaO	0.159	0.086

Table 4. 50 GRAM SOLID TCLP SAMPLES

units are in ppm

SAMPLE ID	Ag	Cd	Cr	Ni	Pb
A	<D.L.	0.055	0.031	<D.L.	<D.L.
B	<D.L.	<D.L.	0.032	<D.L.	<D.L.
C	<D.L.	<D.L.	0.032	<D.L.	<D.L.
D	0.358	1.65	0.064	0.039	0.599
E	0.241	3.20	0.270	0.088	<D.L.
F	0.286	1.71	<D.L.	0.084	0.486

<D.L.= less than detection limits
A = 25% waste load, 950°C, slow quench
B = 25% waste load, 950°C, fast quench
C = 25% waste load, 1200°C, slow quench
D = 75% waste load, 950°C, slow quench
E = 75% waste load, 950°C, fast quench
F = 75% waste load, 1200°C, slow quench

Table 5. TCLP SIZE REDUCTION COMPARISON

units are in ppm

SAMPLE ID	Ag	Cd	Cr	Ni	Pb
A-2	<D.L.	0.052	0.031	<D.L.	<D.L.
B-2	<D.L.	0.071	0.040	<D.L.	<D.L.
C-2	<D.L.	0.069	0.040	<D.L.	<D.L.
A-3	<D.L.	0.143	0.065	0.042	<D.L.
B-3	<D.L.	0.155	0.053	0.137	<D.L.
C-3	<D.L.	0.086	0.041	0.147	<D.L.

<D.L. = less than detection limits

A-2, B-2, C-2: 1.0mm> Size fraction <9.5mm
A-3, B-3, C-3 : Size fraction <1.0mm

By: R. D. Thiel

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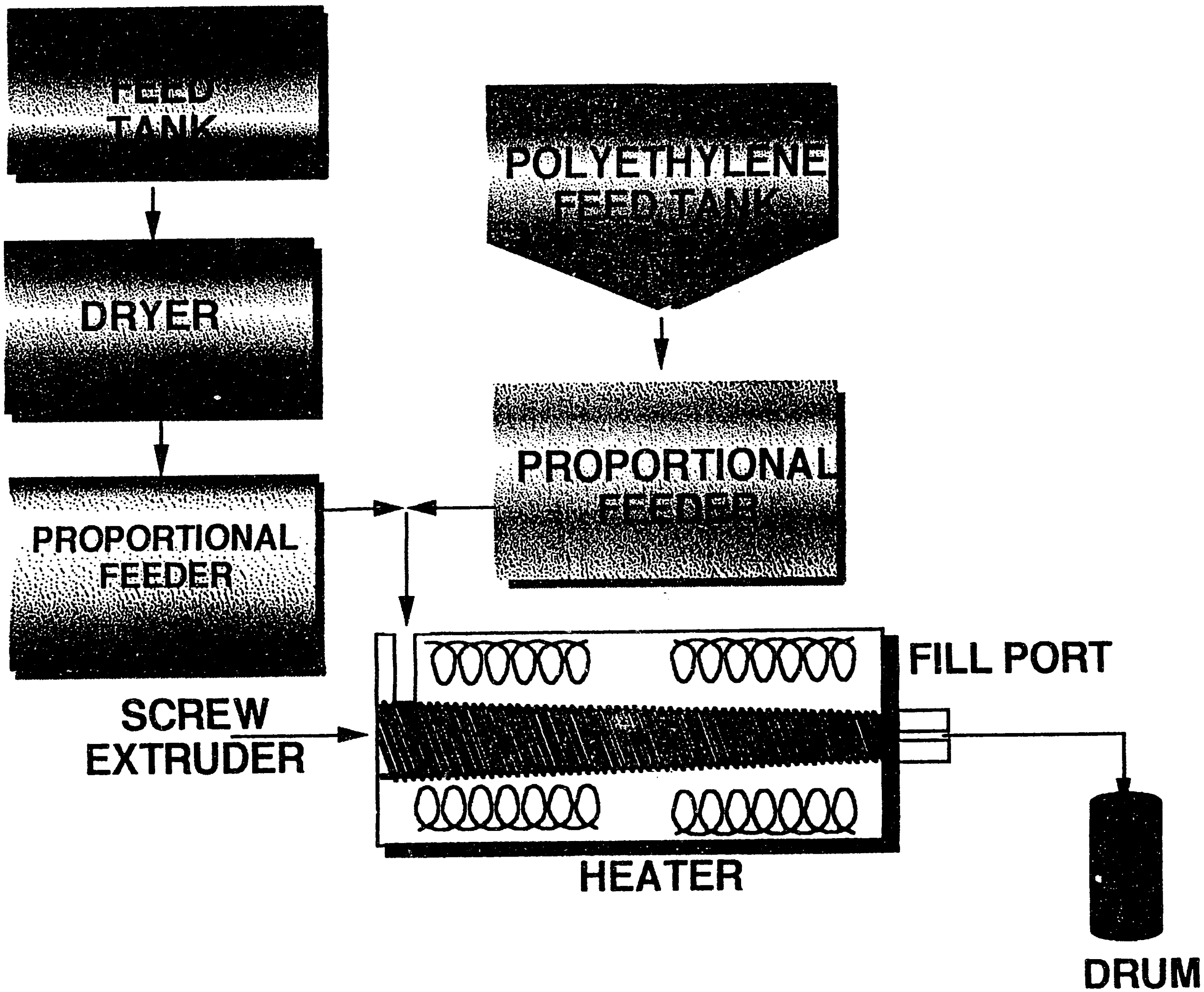
INTRODUCTION

Microwave melting and polymer extrusion stabilization of mixed waste forms results in monoliths formed in 30 gallon stainless steel drums. The 30 gallon drums are over packed in 55 gallon steel drums. Low-level mixed waste destined for the Nevada Test Site is required to pass the Toxicity Characteristic Leaching Procedure (TCLP). This requires size reduction of the monolithic waste form to less than 9.5 millimeter particle size. The methods used to accomplish size reduction can have drastic effects on the TCLP results.

POLYMER SOLIDIFICATION

Extruder Mixing System



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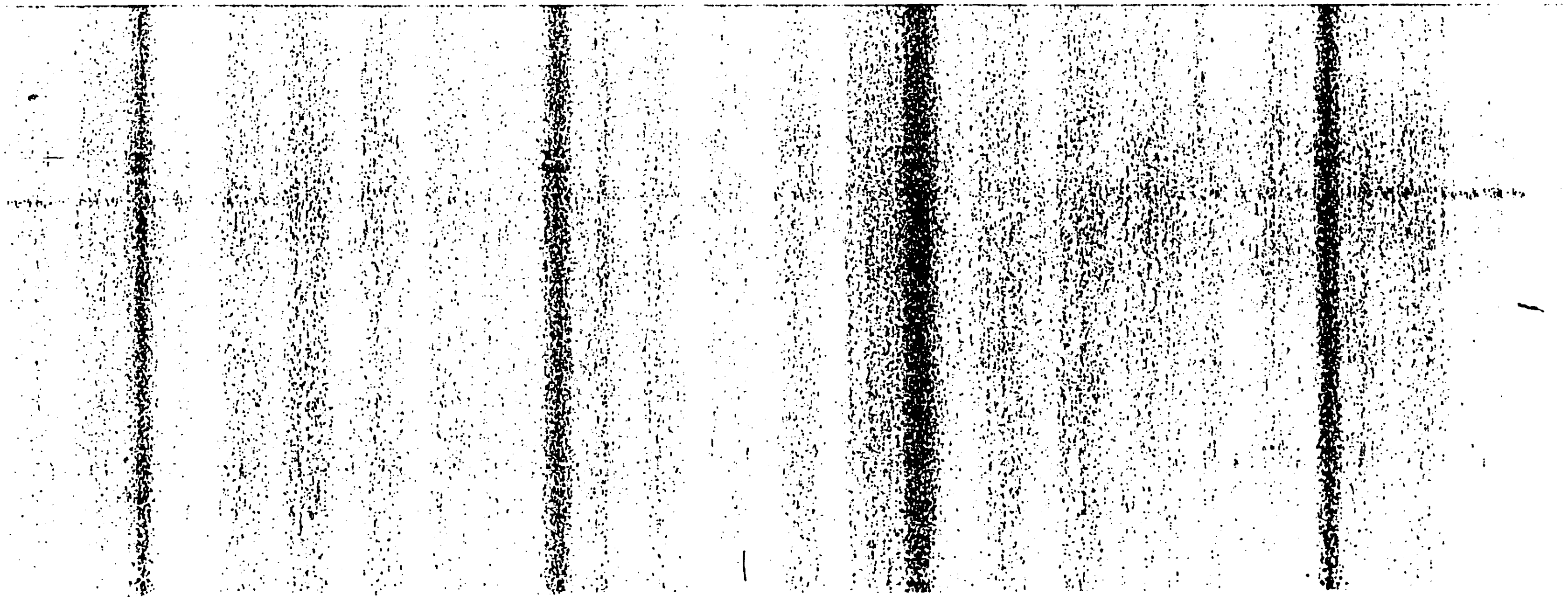
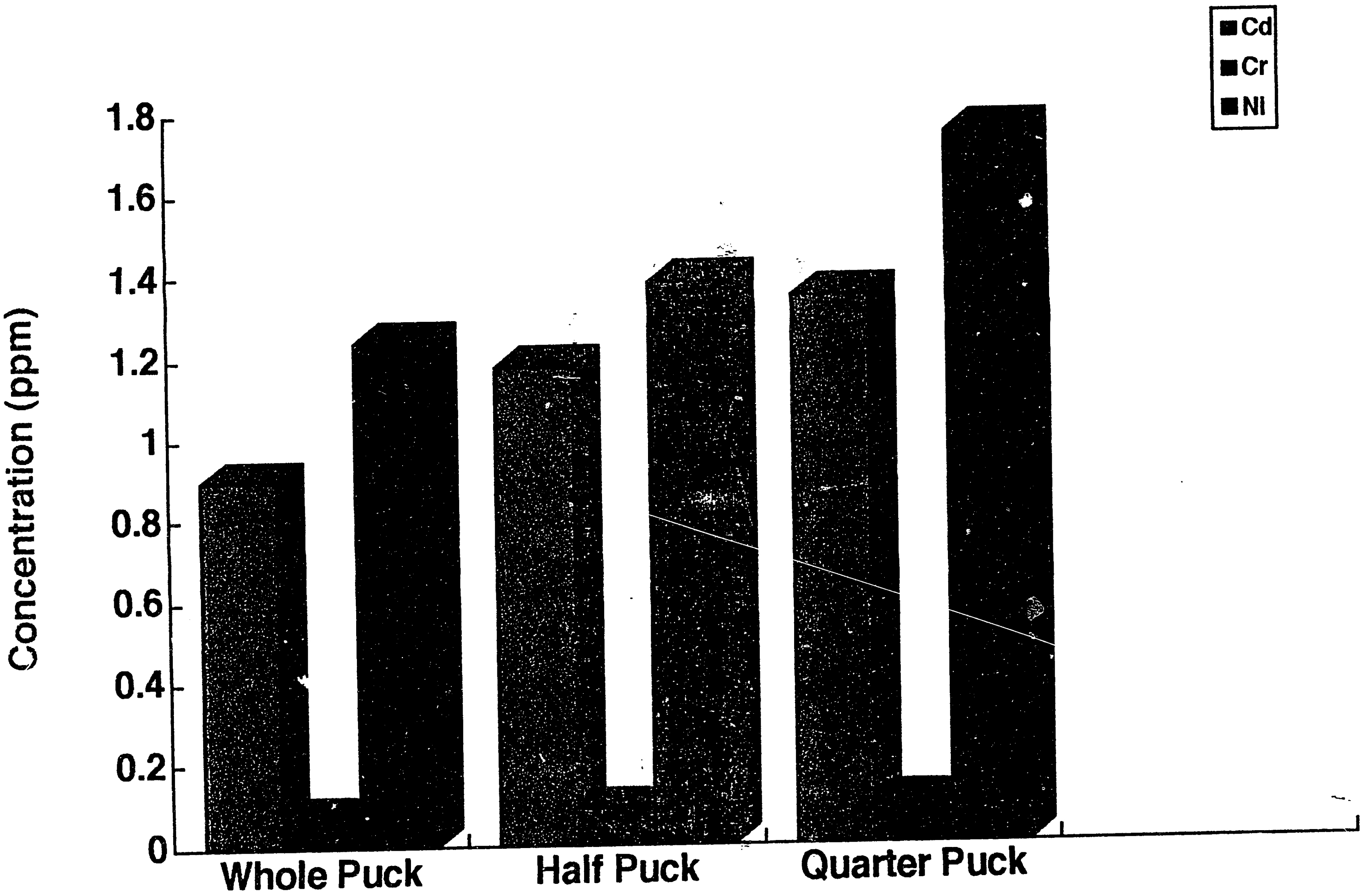
All samples for the polymer encapsulation study were loaded at the 50% level with waste spiked at the 500 ppm level with cadmium, chromium, and nickel.

Polymer solidification, 1" x 2" heated mold samples

This test was conducted to verify increased leaching with increased surface area.



Polymer Size Reduction Study
1 x 2 Heated Molds



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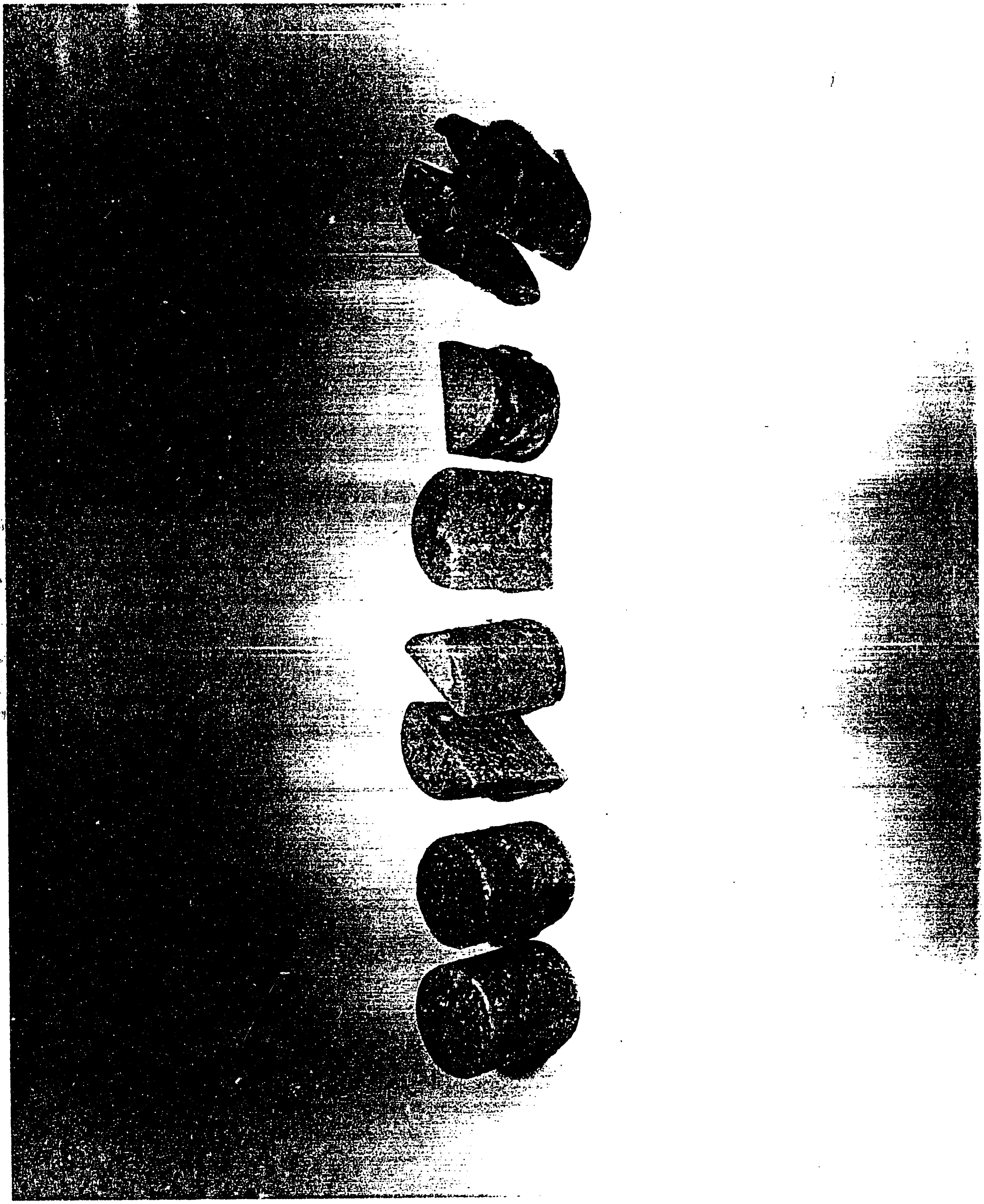
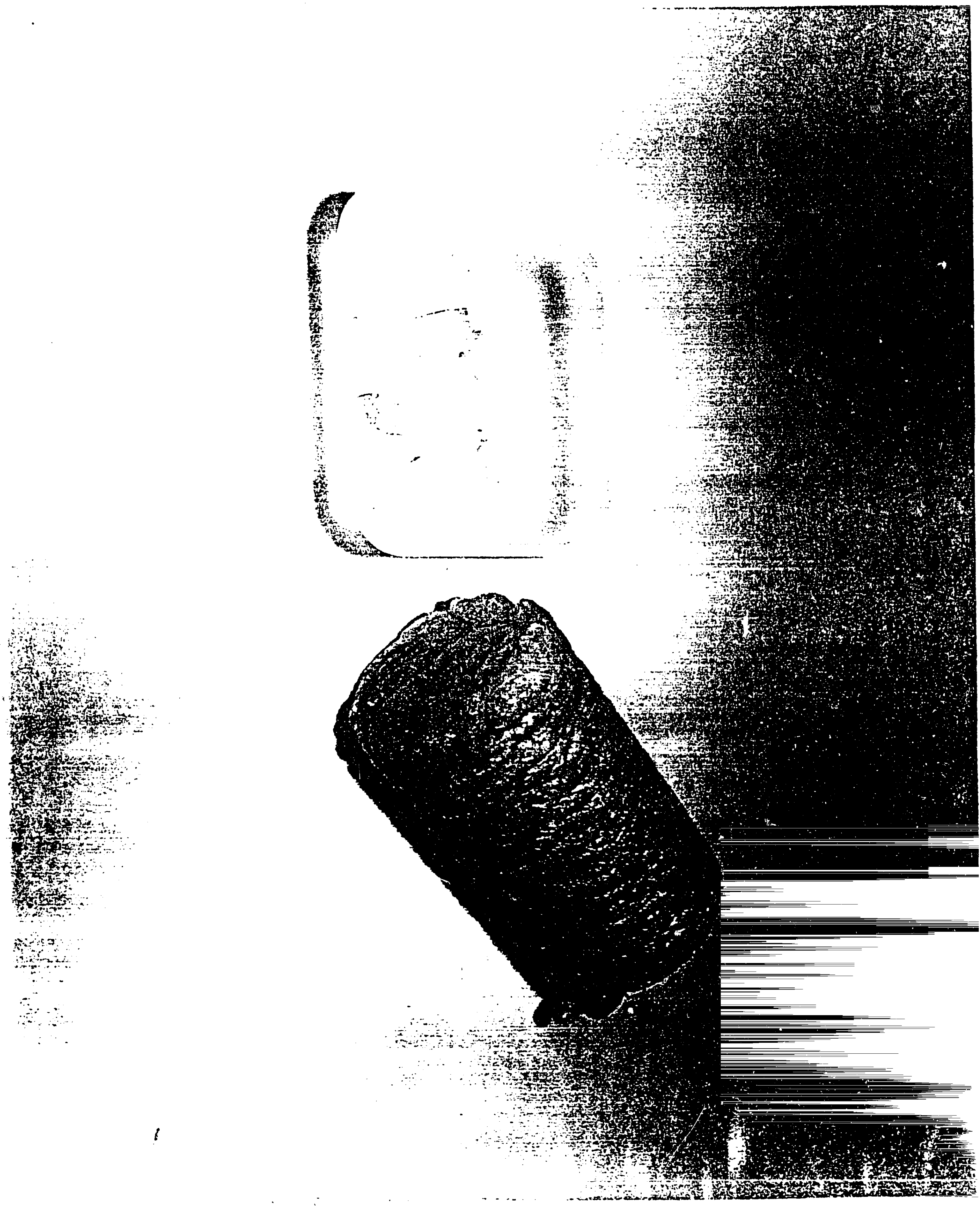
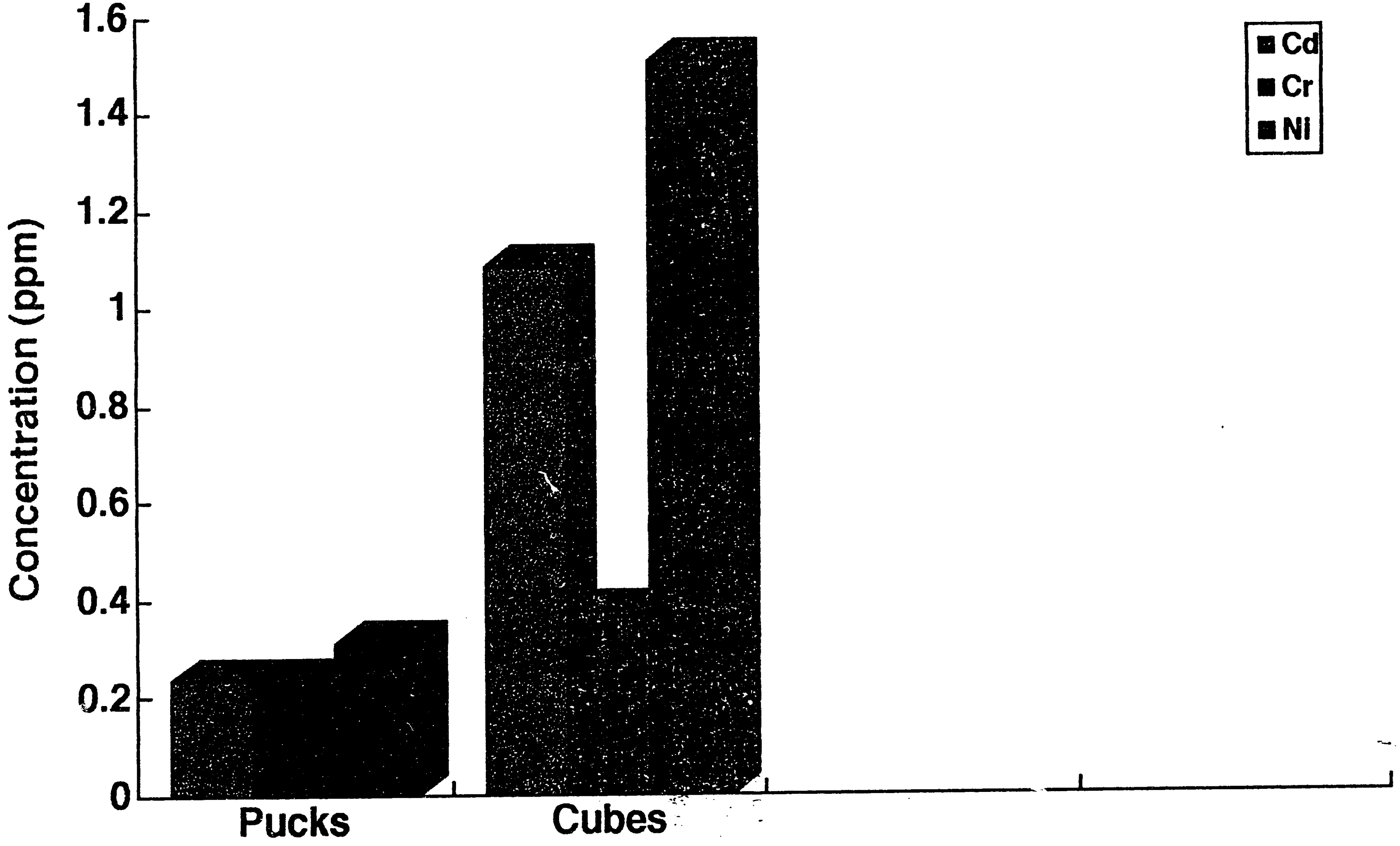




Polymer Size Reduction Study
2 x 4 Nonheated Molds



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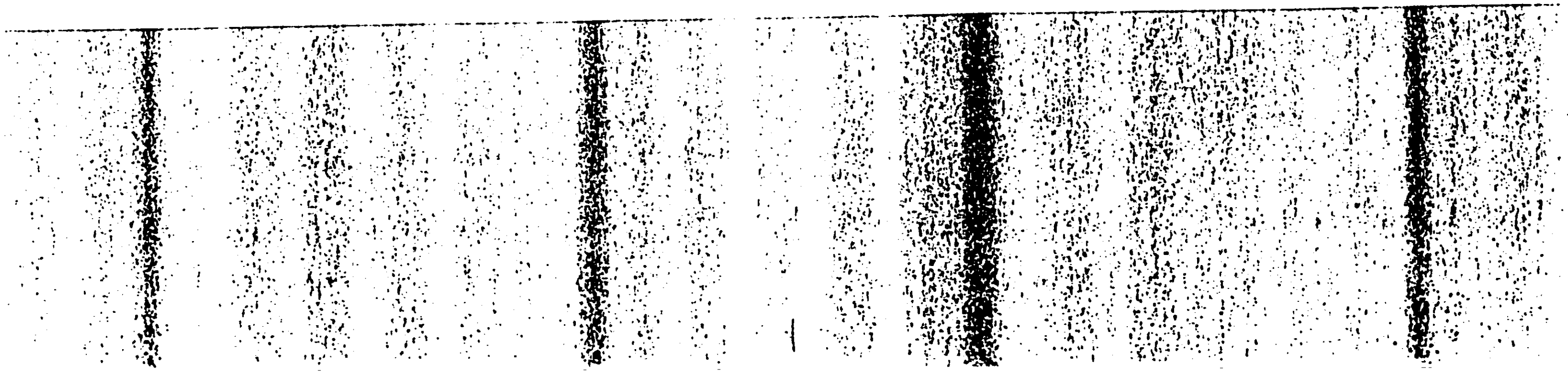
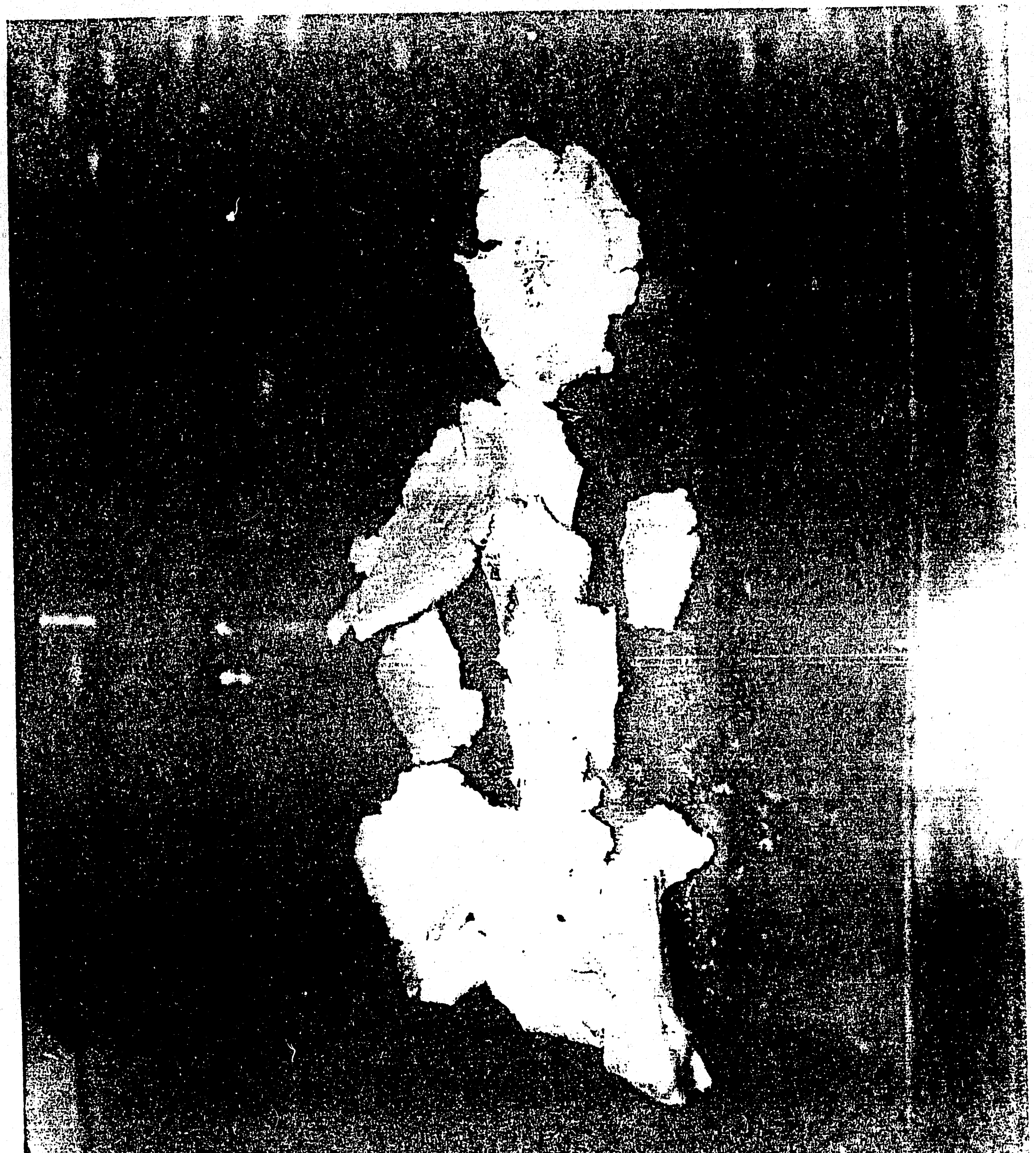
Polymer solidification chemically modified samples

These samples were crushed in a press during size reduction to expose as much chemical modifier to the extraction fluid as possible.

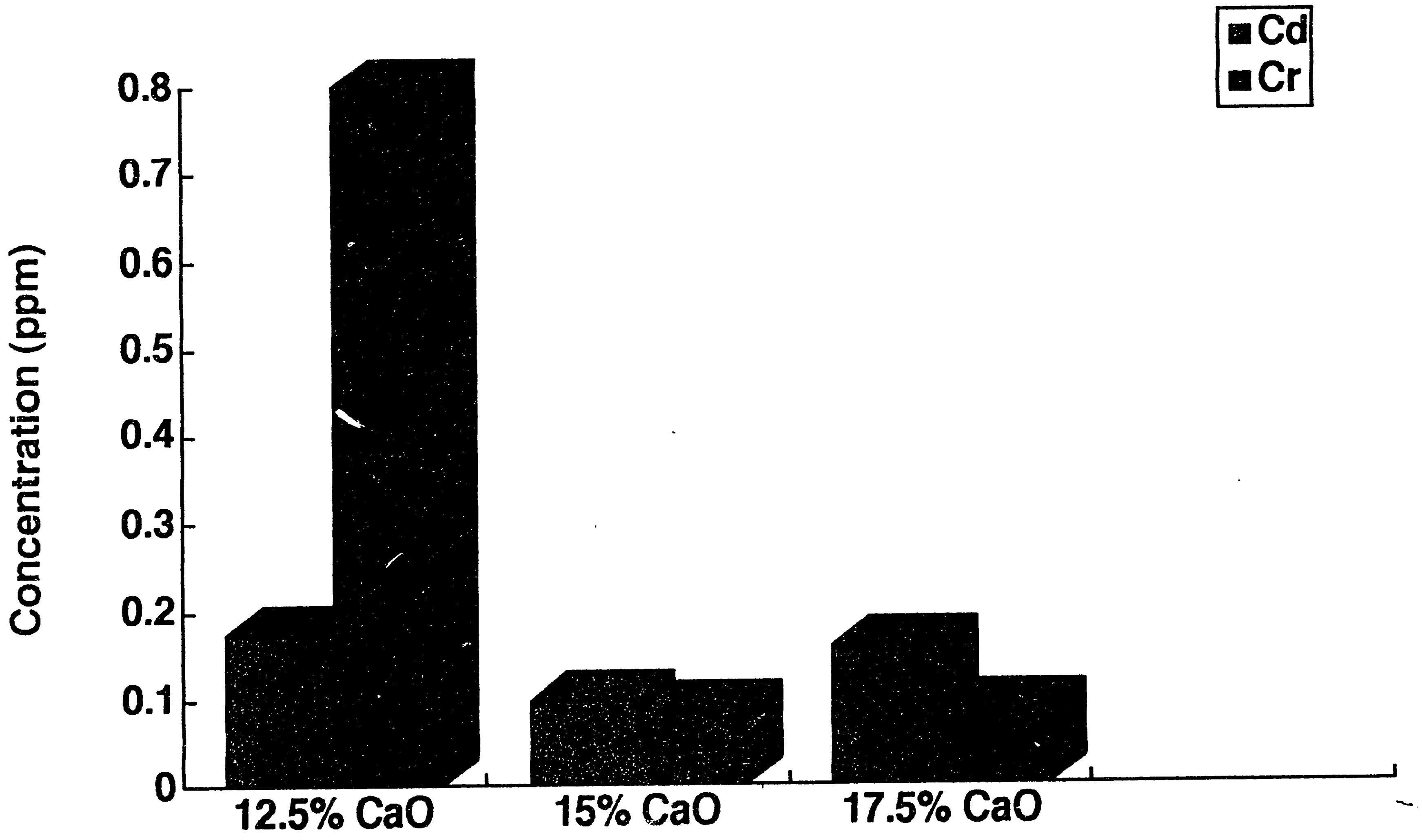
Polymer solidification 2” x 4” nonheated mold samples

The surface of the nonheated mold samples extracted less than the heated mold samples. The cubed samples extracted less than anticipated.





Chemical Modification of Polymer Samples



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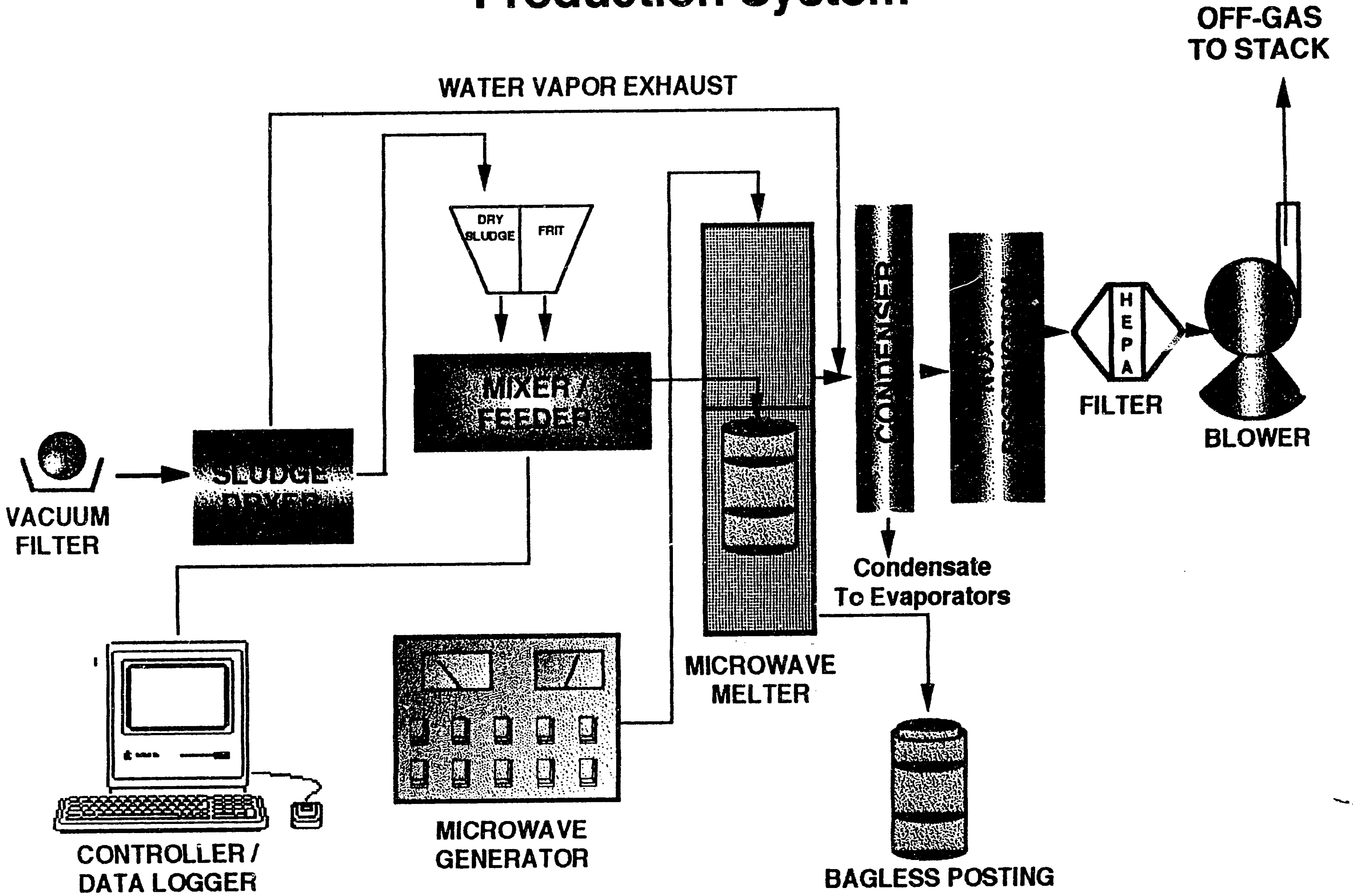
MICROWAVE MELTER
Production System



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The operating conditions and waste loading factor were varied during these runs. The waste was spiked at 500 ppm. 50 gram solid samples that passed TCLP were further size reduced and retested.

Microwave melter

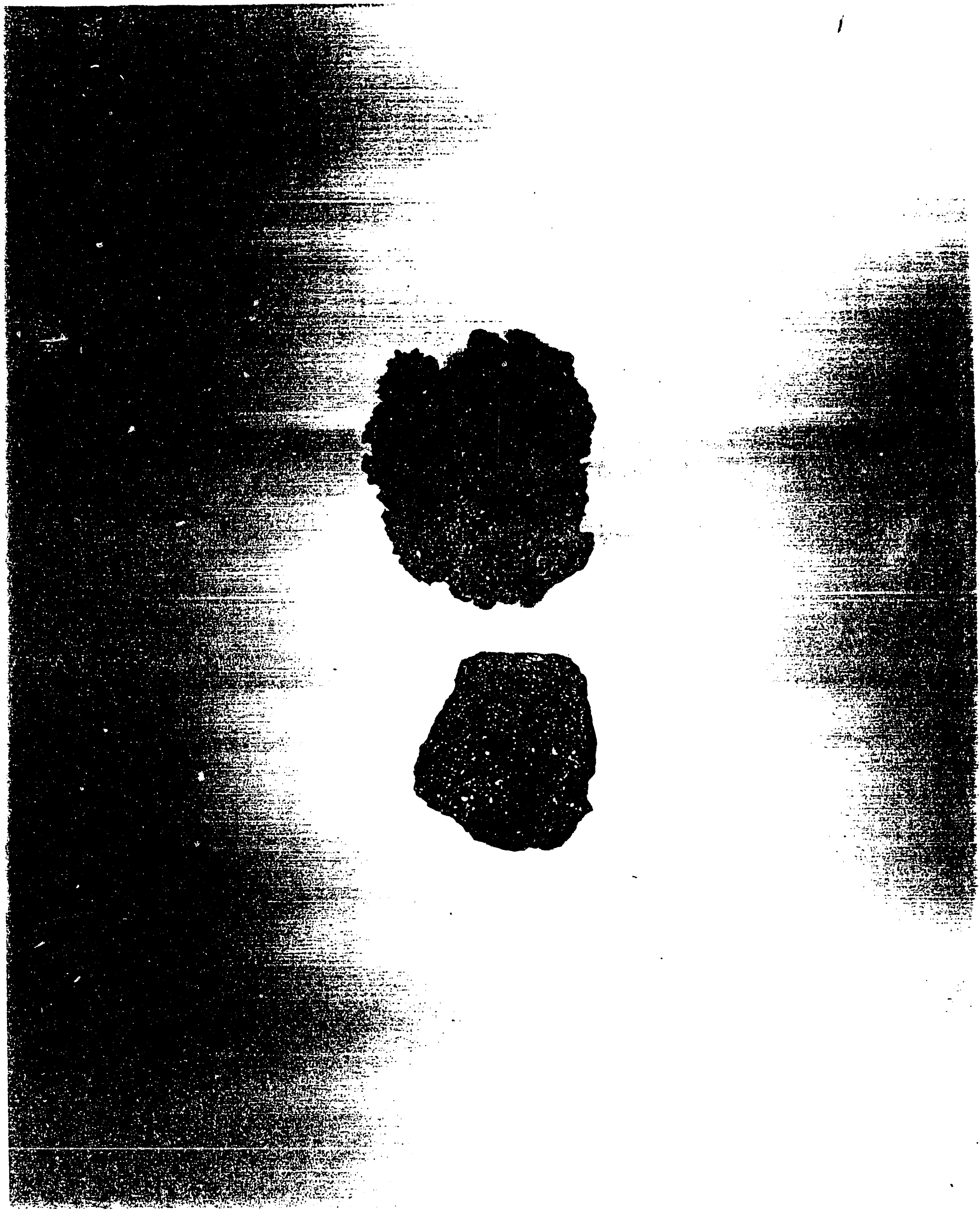
Left: <9.5 mm and >1.0 mm size reduced fraction

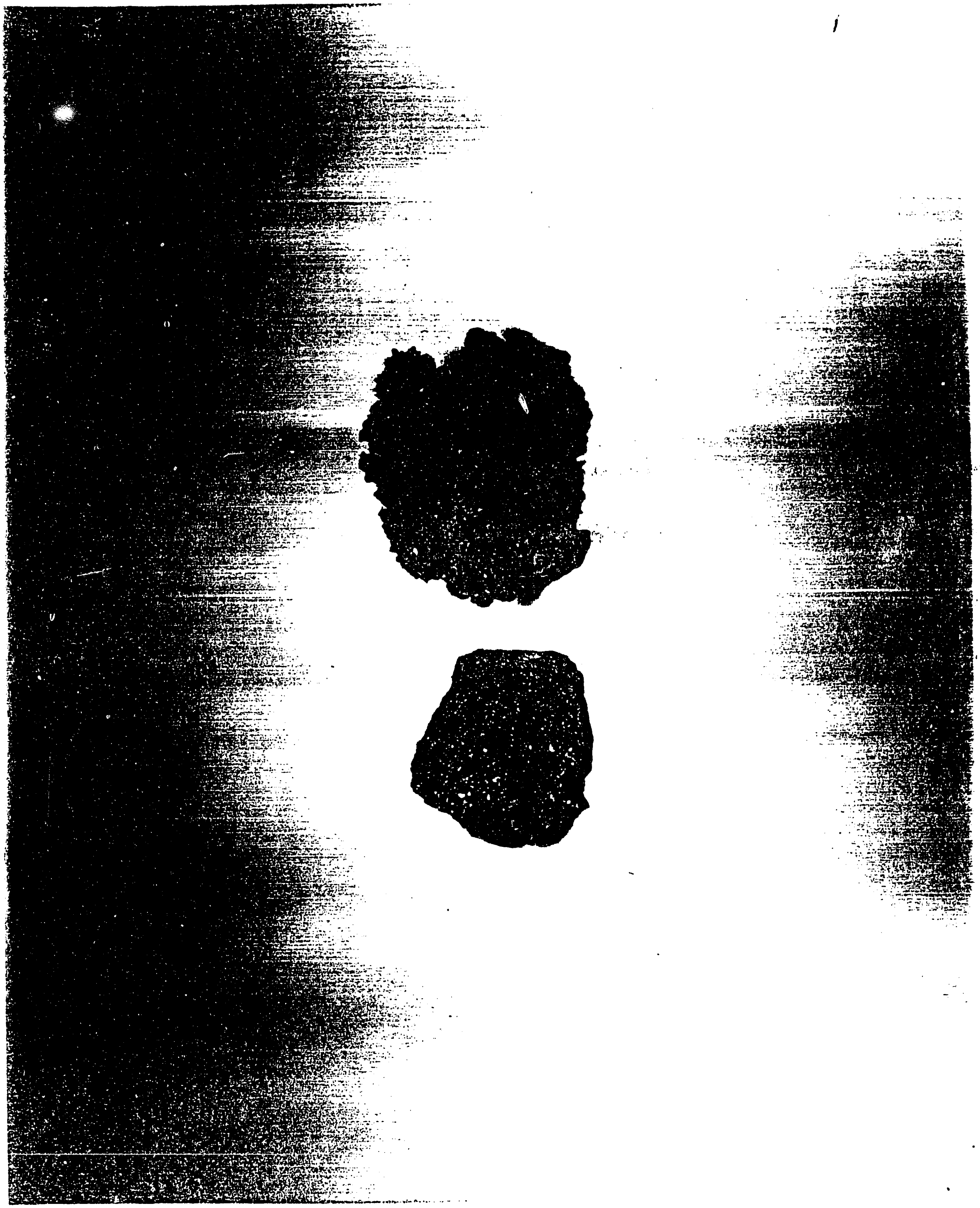
Right: <1.0 mm size reduced fraction

Microwave melter, 50 gram solid samples

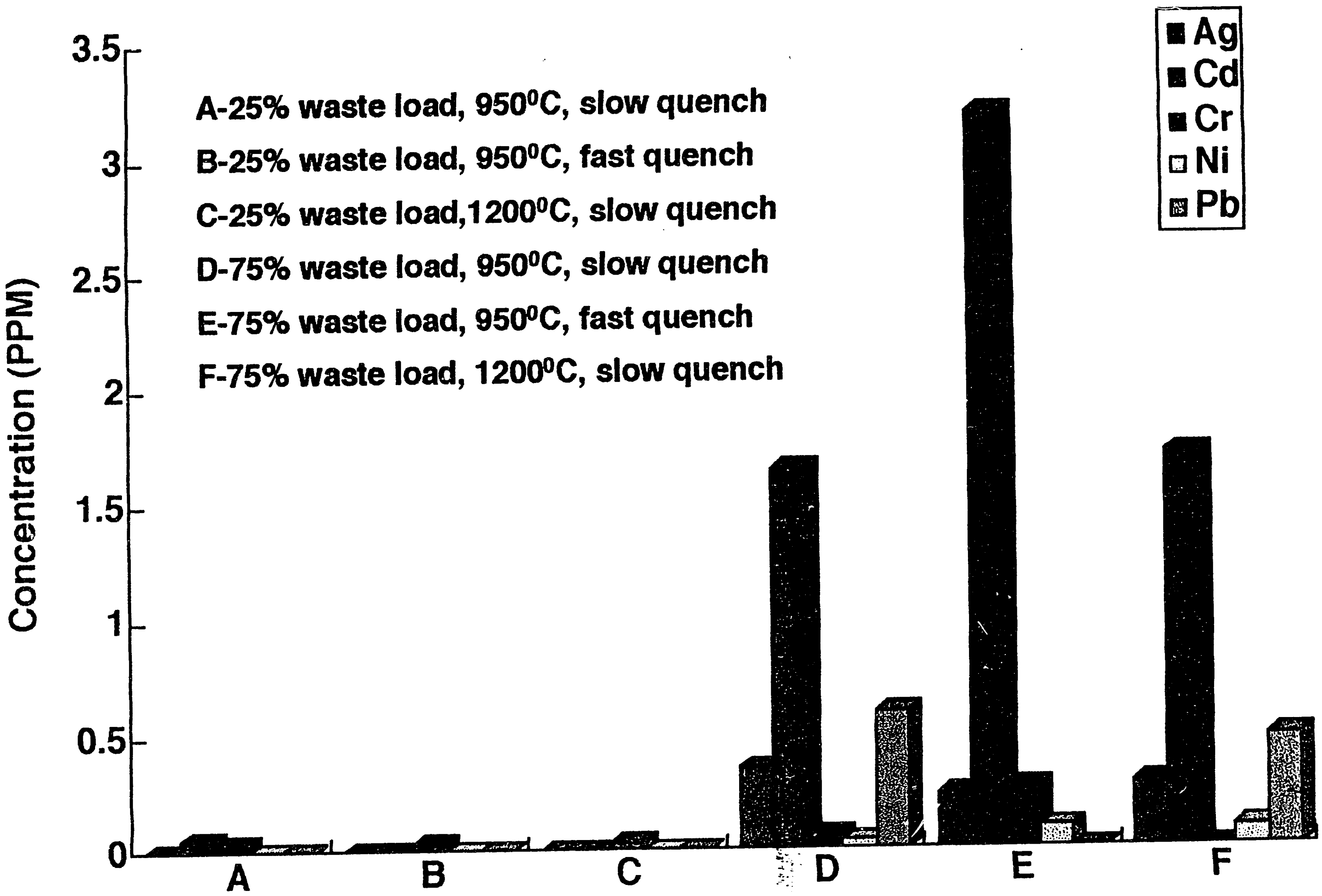
Left: Sample that passed TCLP

Right: Sample that failed TCLP





50 GRAM SOLID TCLP SAMPLES



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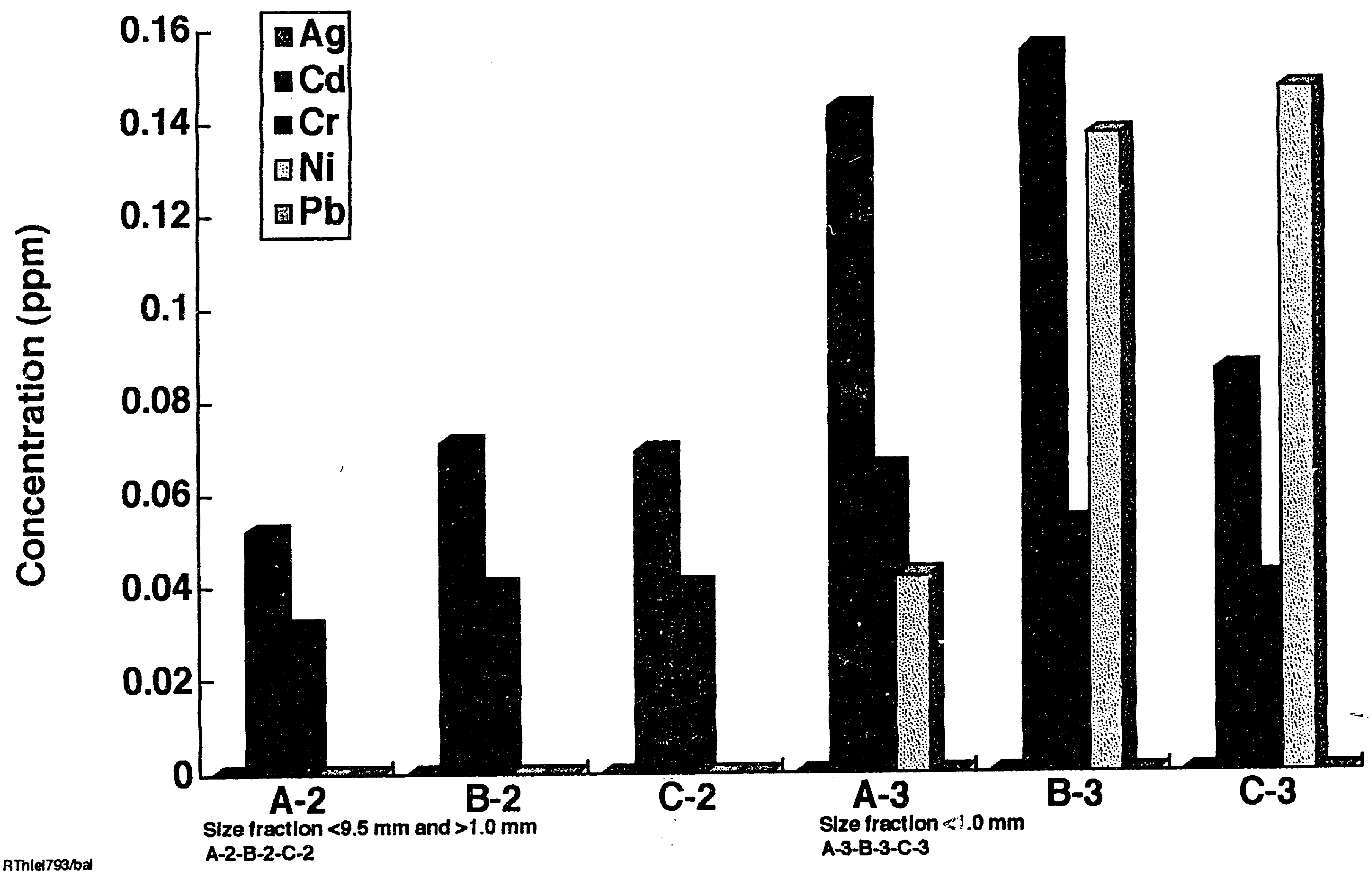
TCLP Size Reduction Comparison



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CONCLUSION

Results for the microwave melting studies indicate that this process, operating under the appropriate conditions, will yield a product that passes the TCLP. However, size reduction must be accomplished with less than 10% of the sample reduced to less than one millimeter.

The results for the polymer solidification studies indicate that size reduction has a larger effect on this process than the microwave melting process. Unlike the microwave melting process, the polymer solidification process stabilizes waste solely by a physical exclusion from the environment. As a sample surface area increases, extractability of RCRA metals increases proportionally. However, sample preparation via pelletizing with rapid cooling of the pellets, and/or chemical modification may overcome this problem.

It is the opinion of this author that, in either case, the size reduction step of TCLP does not fairly represent the performance of either of these stabilization techniques in the environment.

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