UO_2 PELLET MANUFACTURE FOR CANDU FUEL

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ABSTRACT

Nuclear fuel requirements in Canada will reach 2000 MgU by the end of this decade. Operation on this scale has necessitated process changes that have been beneficial with respect to quality and consistency of the UO_2 powder required for the demanding dry pressing pellet fabrication route. The ability to control the physical and chemical properties of UO_2 powder and predict its pelleting behaviour has become increasingly important as the scale of operations increase. To assist this endeavour programs of work have been performed to investigate some of the more serious UO_2 pellet quality problems that have been encountered in recent years. These have included examination of the role of powder agglomerates on pellet processing, the effect of certain chemical impurities on pellet sintering and the effect of long term storage on powder characteristics and pellet fabrication behaviour.

1. INTRODUCTION

One important objective of UO_2 fuel producers has been to improve methods of powder characterization to enable more reliable prediction of pellet fabrication performance and hence avoid or minimize the costs of powder and pellet quality excursions. In addition, if we are knowledgeable of the features of a powder that are responsible for the excursions we will be better able to eliminate them at source or adjust the pellet process to accommodate them. Historically, a major difficulty has been that the more traditional methods of UO_2 powder characterization have not been capable of identifying all types of poor performing powders. In the present context, poor performing powders fall into two main categories viz. those showing physical deviations which prevent the powder being 'dry pressed' into high integrity pellets due to delamination cracking or 'end capping' and those showing chemical deviations involving the presence of an abnormal level of a tramp impurity that can seriously affect sintering behaviour.

2. END CAPPING

A two year research program, sponsored by Ontario Hydro, was undertaken with the objective of identifying the distinctive properties of a powder that are responsible for end capping behaviour. Samples from ten production powder lots that had shown severe end capping, typified by Figure 1, were compared with samples from four reference or standard

powder lots. Comparison of routine powder characterization data (surface area, O/U, bulk density and compressibility) showed no distinctions. Detailed particle size analyses both at WECAN and ERL[1,2] and supportive S.E.M. work had indicated differences in the nature of the powder agglomerates.

Experimental efforts were therefore concentrated on studying the characteristics of individual agglomerates. Agglomerates from the test lots were separated and classified using dry sieving and image analysis techniques. The agglomerates were analysed for particle size distribution, bulk density and fracture strength and also examined using an S.E.M. Particle size distributions were identical to the parent powder lot indicating that the large separated particles were true agglomerates and not unique abnormal particles. Bulk density measurements using a microbalance showed no significant differences between the test and control powders. Measurement of fracture strength using a simple compression rig (Figure 2) showed significant differences between the test and control powders (Figure 3). Examination of the agglomerates using the S.E.M. gave qualitative support to the strength measurements, the weaker agglomerates having a less developed crystallite and neck structure than their stronger counterparts (Figures 4 and 5).

Although all the work described was done on separated large agglomerates, the particle size analysis infers that the results are a manifestation of the general state of agglomeration in the powder lot as a whole; the technique of testing the large agglomerates served as a convenient means of characterizing the agglomeration properties of the lot per se. In support of this hypothesis different size fractions in the range 40-400 μm were separated from an abnormal test lot and subjected to pellet fabrication testing; all fractions exhibited end capping behaviour.

3. TRAMP IMPURITIES

In recent years there has been an increasing number of pellet quality or process performance excursions attributed to the presence of certain minor impurities at less than 100 ppm levels. It is believed that changes in pellet processing methods, particularly increased heating rates during sintering, have resulted in impurity entrapment and modification of diffusion processes responsible for basic sintering mechanisms. For the relatively low levels of impurities involved the observed effects are drastic, involving in one case grain growth changes of two orders of magnitude and in the other cases density depressions in excess of 1%.

The first incident occurred during the introduction of the newly developed 'AU' process by Eldorado Resources Limited[3]. This process included controlled additions of sulphuric acid to increase the reactivity of the UO_3 intermediate and resulted in above normal levels of sulphur in the powder. Sintering of this material in modern furnaces resulted in

exaggerated grain growth (> 600 μm) and density depression. Laboratory testing[4] subsequently demonstrated excessive grain growth at sulphur levels > 35 ppm and moderate heating rates.

In the second incident a water treatment problem resulted in the presence of abnormal levels of sodium (> 10 ppm) in the UO_2 powder and a subsequent sintered density depression of 0.5 - 1% during pellet processing. A limited laboratory experiment was performed to examine the influence of sodium on UO_2 sintering behaviour. Samples contained three levels of sodium (3, 35 and 60 ppm) were sintered at two heating rates; the results (Figure 6) show significant density depression as a function of both sodium content and heating rate.

The last example involved the presence of abnormal levels of phosphorus (> 20 ppm) in the powder resulting in density depressions in excess of 1%. Subsequent heating rate sensitivity tests performed at 200, 350 and 500°C/hr. using a laboratory furnace confirmed the effect for phosphorus contents in the range 30-55 ppm (Figure 7).

4. UO_2 POWDER AGEING

An extended three year test, sponsored by Ontario Hydro, was recently completed to investigate the effect of storage time of UO_2 powder on powder characteristics and pellet fabrication behaviour. The powder lot, in standard containers, was stored in an unheated enclosure; at four month intervals a powder drum was withdrawn, sampled for characterization tests and subjected to a full scale pellet fabrication test. The results of the three year program are summarized in Figure 8. With one exception, no significant changes in the powder were observed for both properties and pellet fabrication performance. The one exception was O/U ratio which progressively increased to 2.23.

5. SUMMARY

Agglomerate properties have been identified as the principal characterizing feature for pellet end capping behaviour.

Low concentrations of tramp impurities in ceramic grade UO_2 powder can have very significant effect on pellet sintering behaviour in modern furnaces.

Ceramic grade UO_2 powder produced by Eldorado Resources Limited is not adversely affected after a three year storage period.

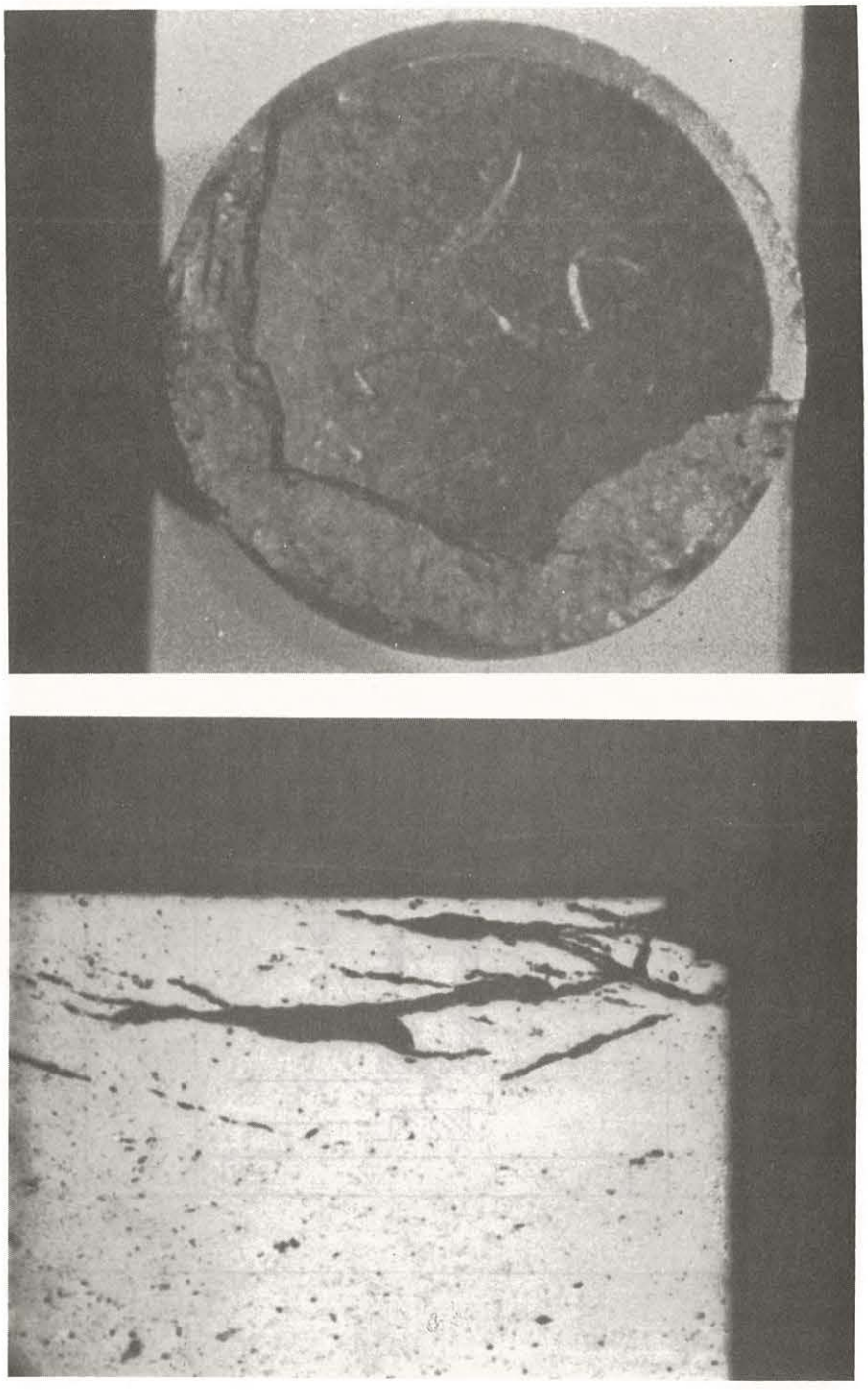
6. REFERENCES

(1) T. W. Zawidzki and I. J. Itzkovitch, "Yellow Cake to Ceramic Uranium Dioxide: A Review of the Process, Problems and Solutions", 4th Annual Conference, CNS, June 1983.

(2) R. C. Burk, T. W. Zawidzki and P. S. Apté, J. Am. Ceram. Soc. 66 (1983)815.

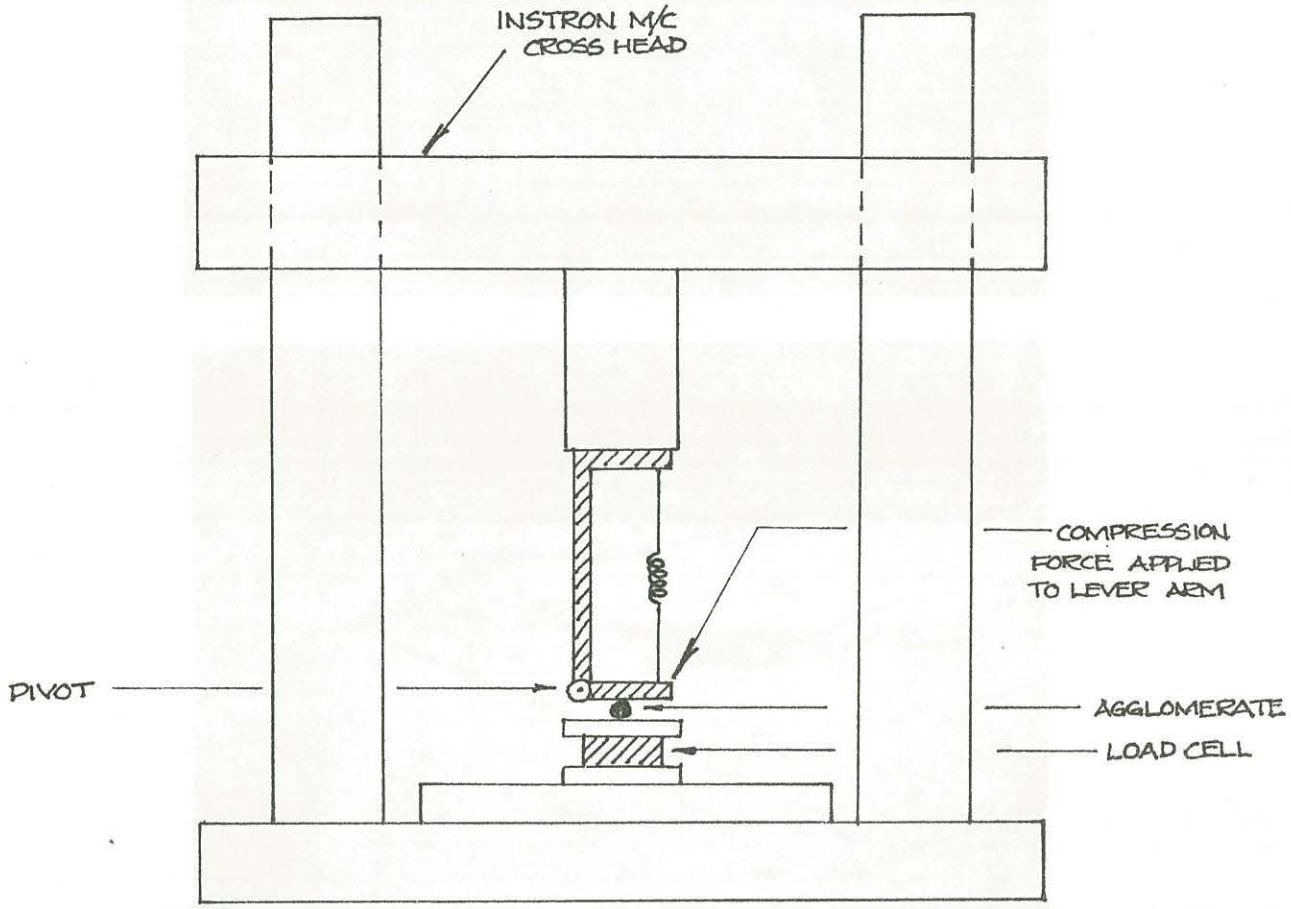
(3) T. W. Zawidzki and B. C. Smart, Australian Patent No. 493398 (1978).

(4) T. W. Zawidzki, P. S. Apté and M. R. Hoare, J. Am. Ceram. Soc. 67 (1984)361.



TYPICAL EXAMPLE OF END CAPPING DEFECT

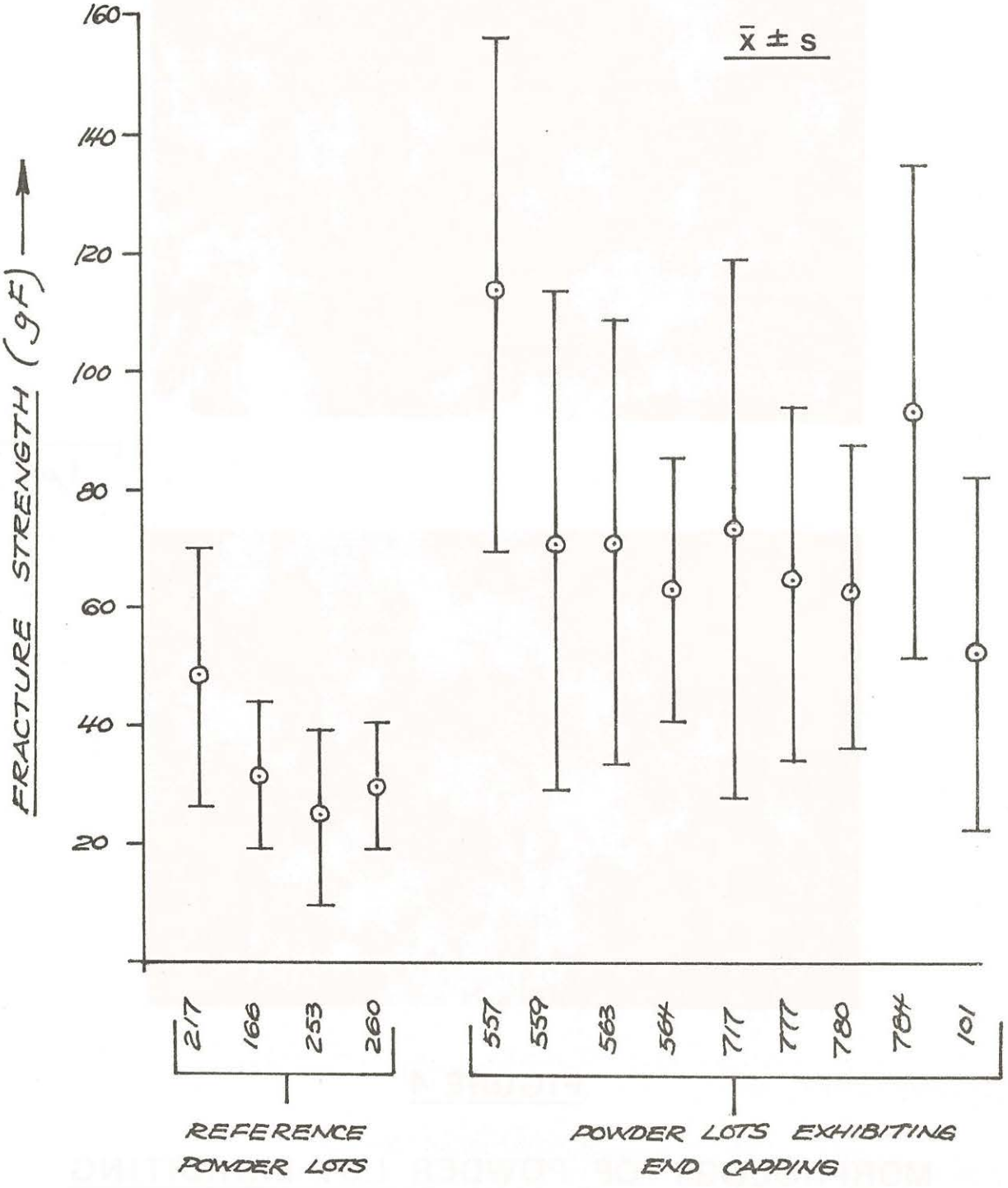
FIGURE 1



SCHEMATIC OF AGGLOMERATE STRENGTH

TEST FIXTURE

FIGURE 2



STRENGTH OF AGGLOMERATES

FIGURE 3

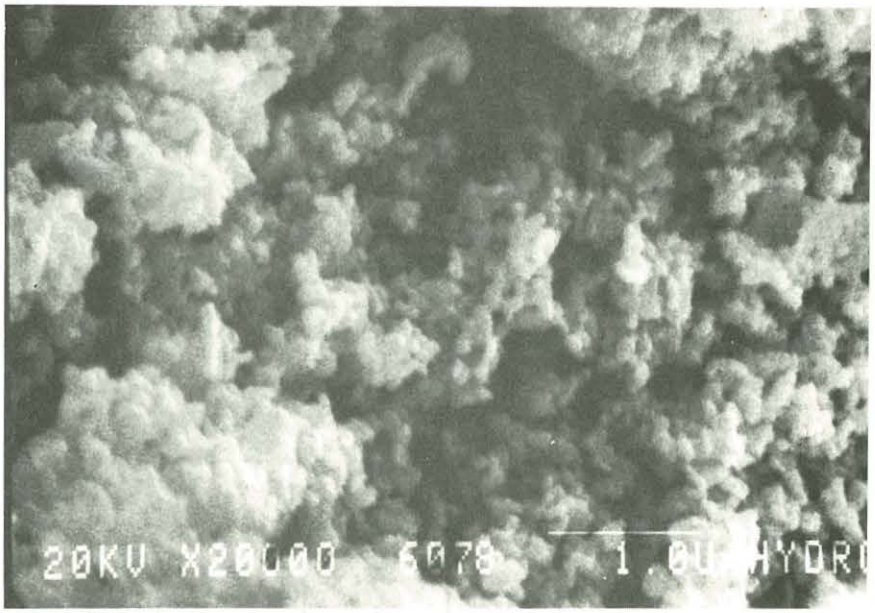
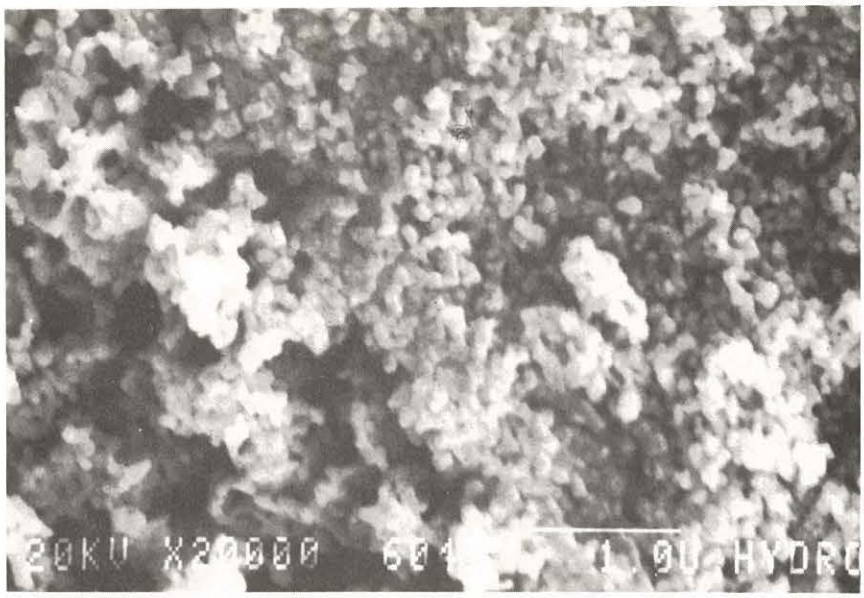


FIGURE 4

MORPHOLOGY OF POWDER LOT EXHIBITING GOOD COMPACTION BEHAVIOUR

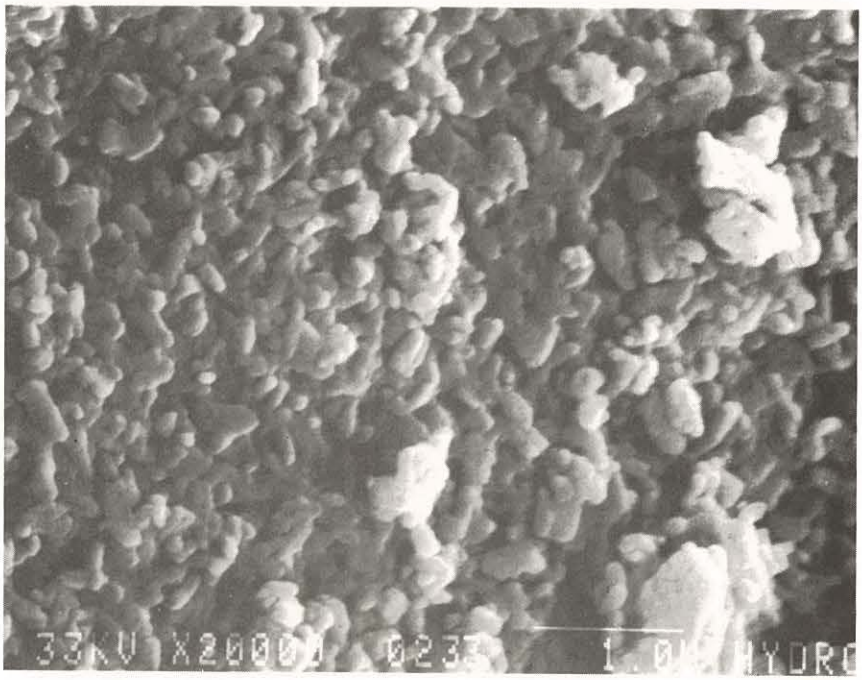
LOT 217 x 20 K



LOT 557

x 20K

1 μm



LOT 559

x 20 K

FIGURE 5

MORPHOLOGY OF POWDERS EXHIBITING END-CAPPING BEHAVIOUR

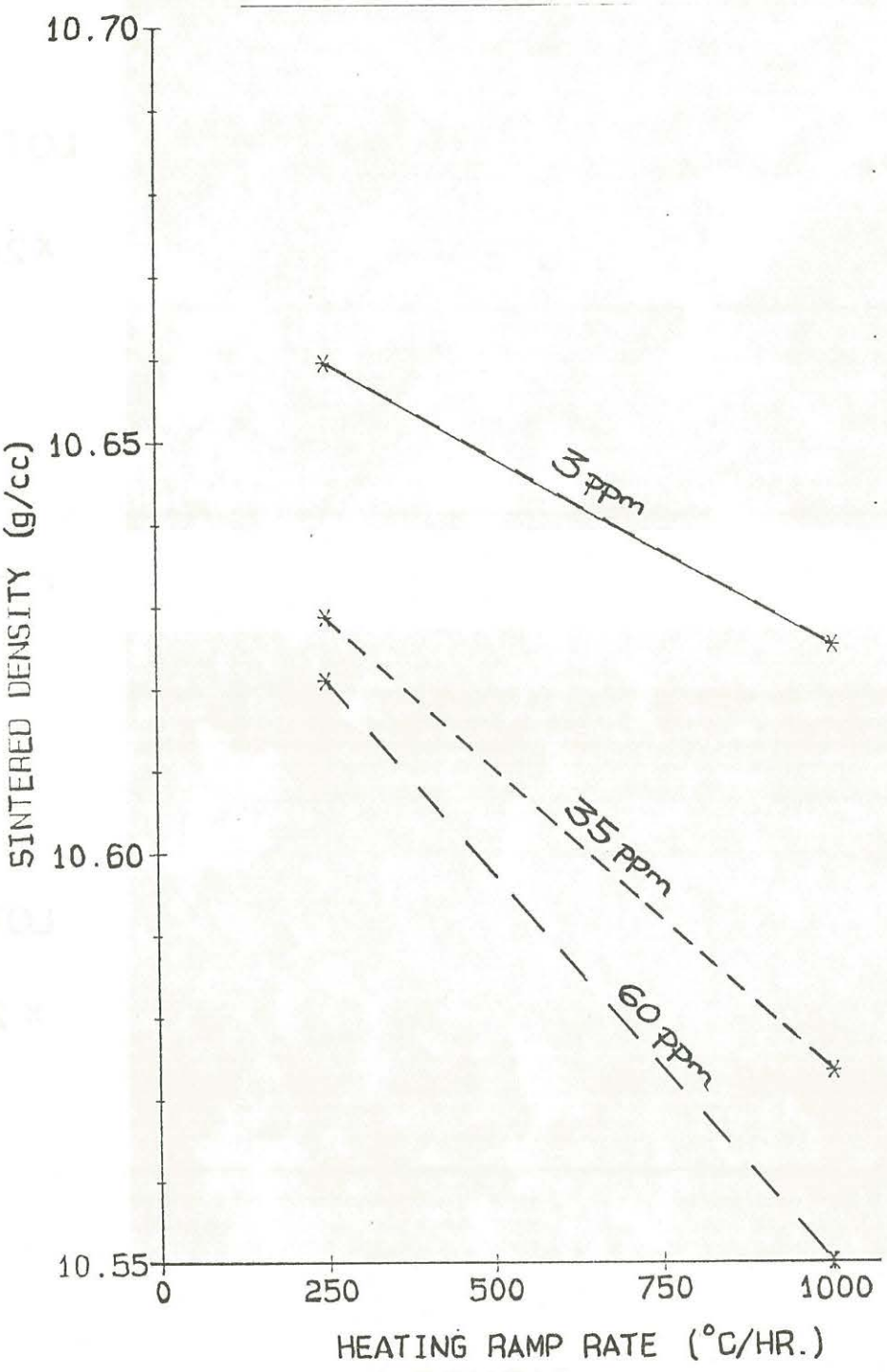
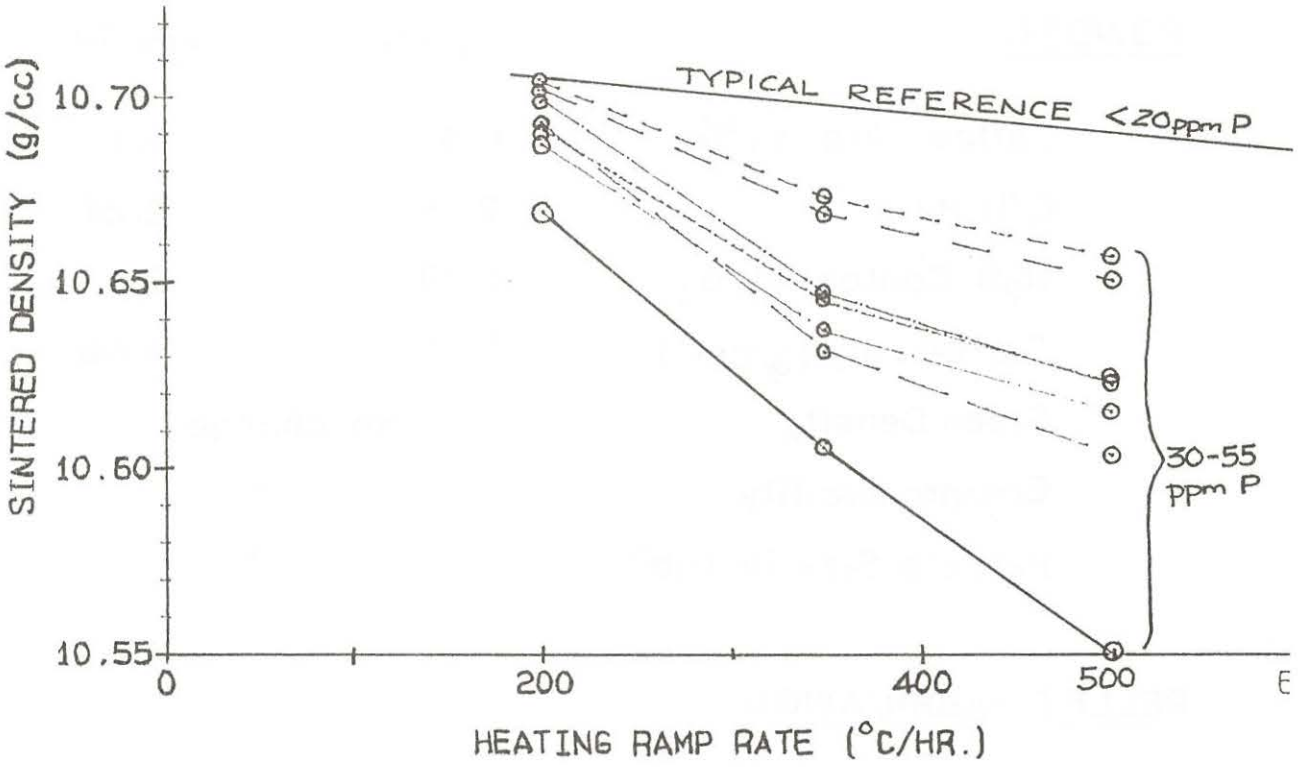


FIGURE 6

Effect of Low Level Sodium Impurity on UO_2 Sintered Density



Effect of Low Level Phosphorus Impurity on UO_2

Sintered Density

FIGURE 7

(P analysis, courtesy of ERL)

POWDER	START	FINISH
Surface Area (m^2/g)	6.4	6.4
O/U Ratio	2.15	2.24
H_2O Content (w/o)	0.19	0.22
Tap Density (g/cm^3)	2.07	2.08
Green Density	no change	
Compressibility	"	"
Particle Size Distrib^n	"	"

PELLET FABRICATION		
Integrity	Accept	no change
Density	no change	
Microstructure	"	"

UO_2 POWDER AGEING PROGRAMME

Test Results

FIGURE 8