THE PROPERTIES OF QUADRUPLE MELTED ZR-2.5NB PRESSURE TUBES

G.D. Moan, A.M. Babayan and J.R. Theaker
Atomic Energy of Canada Limited, Canada

ABSTRACT

Chlorine is one of the impurities present in Zr material produced by the Kroll process and tests have shown that it has a detrimental effect on the fracture toughness of Zr-2.5Nb. It has also been shown that pressure tubes made from multiple melted Zr-2.5Nb ingots have superior fracture toughness properties when compared with those produced from double melted (DM) material. Quadruple melting (QM) has been used for Zr-2.5Nb material produced by the Kroll process and the fracture toughness benefit has been obtained. The paper reviews the properties of pressure tubes made from QM ingots and shows that the other properties are not affected by the use of QM or DM for the ingots.

1.0 INTRODUCTION

Most Zr-2.5Nb pressure tubes in CANDU reactors are made from double melted ingots produced from Zr sponge obtained by the reduction of $ZrCl_4$ by Mg in the Kroll reaction

$$ZrCl_4 + 2Mg \rightarrow Zr + 2MgCl_2 \qquad (1)$$

One of the impurities is chlorine (Cl). Work carried out in the early 1990's showed that the fracture toughness properties of pressure tubes increased as the concentration of Cl decreased as shown in Figure 1. For ingots made up from sponge produced by the Kroll process it was found that the Cl could be kept to low concentrations by multiple melting of the ingots (Theaker et al., 1994) and that improved fracture toughness values were found in material that had been melted 4 times (quadruple melting, QM). It would, thus, be advantageous from a fracture toughness perspective to have pressure tubes made from QM ingots. The present paper contains fracture toughness data showing the benefit of using QM to give low Cl concentrations and summarizes the results of a study carried out to show that the other properties of the pressure tubes were not detrimentally affected by the use of QM material. If Zr material produced by other processes does not contain Cl, it is not necessary to use QM to improve the fracture toughness.

2.0 PROCESSING OF PRESSURE TUBES

Most Zr-2.5Nb pressure tubes installed in CANDU units were made from ingots that had been melted twice (double melted, DM). As summarized in Figure 2, ingots, with diameters about 600 mm, were hot forged from 1015°C to a final diameter of about 200 mm. The forged material was then machined to produce hollow billets with length 560 mm, 200 mm OD and containing a trepanned full length hole 100 mm ID. These dimensions mean that about 25% of the forged material (i.e., the trepanned cores) was not used in the production of the pressure tube. Thus, at least 25% of the material from each ingot was available for recycling in later ingots. Information supplied by the ingot manufacturer shows that many ingots contained 20-60% recycled material and that some contained 0 or 100% recycled material. The ingots made from 100% recycled material are of special interest as the material in them was melted 4 times, so that they are, in effect, QM. This means that the properties of the pressure tubes made from them will be representative of those expected in tubes made from QM ingots.

The trepanned billets were extruded at 815°C, and the extrusions thus produced were cold drawn 25-28% in 2 passes. The pressure tubes were then machined to size, autoclaved at 400°C and, during inspections, several dimensions and properties were measured to confirm that the pressure tubes met AECL specifications. Data from these measurements were included in the history dockets.

3.0 CHANGES OCCURRING DURING REACTOR SERVICE

During reactor service, pressure tubes are exposed to the effect of D_2O coolant, neutron flux, temperature in the range 260 to 310°C and internal pressure so that they

i) undergo dimensional changes from creep and growth,

ii) are oxidized on the inside surface, and pick up deuterium as a result of the oxidation reaction, and

iii) show changes in tensile strength and in the delayed hydride cracking (DHC) behaviour.

These changes are monitored during in-reactor inspection programs and in the inspections and tests carried out on pressure tubes removed from reactor as part of surveillance programs or during the Large Scale Fuel Channel Replacement (LSFCR) programs. To determine if the number of times that the ingot material has been melted (i.e., DM or QM) has an effect on the other (i.e., non fracture toughness) properties, large databases containing results from these tests and inspections have been reviewed.

4.0 REVIEW OF DATA

The following 3 sections review the pre-, in- and post-service data.

4.1. Pre-service Data

The axial tensile properties are measured at 300°C using samples prepared from the front (weaker) end of the tubes and the data provided in the pressure tube history dockets were used to prepare histograms to show the distribution of the values for different reactor orders.

Since the interest in the study was differences that could be attributed to DM or QM ingots a database containing the properties of almost 2000 tubes made about 1980 was used. Over 200 tubes produced from ingots made up from 100% recycled material, (i.e., in effect QM ingots) were identified and the data sorted into QM and DM groups. Note that tubes with less than 100% recycled material are considered as DM. The histograms in Figures 3, 4 and 5 (summarized in data set A in Table 1) show the similarity in the distribution of the YS, UTS and Elongation distributions for the QM and DM tubes. In other reactor sets studied the YS, UTS and Elongations were slightly higher for the DM tubes. Thus differences in YS, UTS and Elongations were small and in some reactors in favour of the QM tubes, in other units in favour of the DM tubes.

The results from the autoclave ASTM G-2 corrosion test for the 2000 tubes in Figure 6 show that the two distributions are similar as indicated in data set A in Table 1. The results from these corrosion tests indicate that the DM material is slightly better, but in other corrosion tests the QM material appears slightly better.

Thus, the tensile and corrosion data measured during tube manufacture indicate that there is no systematic difference in the tube properties that can be attributed to the number of times that the ingots were melted to produce the QM and DM materials.

4.2. In-reactor Measurements of Axial Elongation

During service, changes in the axial length of fuel channels are monitored and the average elongation rate can be calculated. Databases with data for up to 17 years have been examined for two stations, one containing data from 2150 fuel channels and the other containing data from 780 channels. The results for data sets B and C in Table 1 show that there is very little difference between the mean values for the axial elongation rates of the QM and DM materials in each of the 2 stations.

4.3. Post-service Measurements

The different measurements carried out on pressure tubes after removal from service are summarized in the following sections.

4.3.1. Oxide Thickness Measurements on the Inside Surface

During service the hot D_2O coolant oxidizes the inside surface of the pressure tube and leads to an increase in the oxide thickness at a rate that depends on the local temperature and power. The reaction can be described by the equation:

$$ZrCl_4 + 2Mg \rightarrow Zr + 2MgCl_2 \qquad (1)$$

The oxide thickness has been measured on many sections of pressure tube, after their removal from service, using optical metallography or Fourier Transform Infra Red (FTIR) Spectroscopy. The oxide thickness database from the tubes inspected after removal from Pickering Units 3 and 4 during LSFCR has been examined. Since the database contained oxide thickness data measured on pressure tube rings taken from different axial locations along the tubes it was found necessary to sort the oxide thickness data into 6 groups representing material from the 3 reactor power zones and 2 arbitrarily selected temperature regimes in each channel. The temperature regimes used were the inlet half of the pressure tube with temperatures approximately 250 to 270°C, and the outlet half with temperatures approximately 270 to 291°C.

The data set D in Table 1 summarizes the mean and standard deviations calculated for the 6 groups. The data show that there is no systematic difference in the oxide thickness that can be attributed to the QM or DM material.

4.3.2. Deuterium Concentrations at Different Axial Locations

During reactor service, a fraction of the deuterium (D) byproduct from the reaction given in equation (2) is picked up by the pressure tube. For Zr-2.5Nb in CANDU units, the fraction is about 5%.

The D concentration database with the following data has been examined:

1. in tubes removed for surveillance purposes the D concentration is measured in through-wall pellet samples, typically, at 4 circumferential orientations at 4 axial locations along the tube.
2. in tubes remaining in service, scrape techniques are used to remove thin slices of the tube from the top inside surface at typically the same axial locations, with care being taken to ensure that the oxide layer is removed first.

Since the D concentration in a tube varies with the axial location (or temperature) and reactor power zone, the data were subdivided into 6 groups to include the 3 power zones and the inlet and outlet halves of the tubes. The temperatures in the inlet halves of the tubes were 254 to 283°C and in the outlets 284 to 313°C. The D database contained data from several different units, and the above temperature ranges represent those found in the database. The temperatures in an individual fuel channel did not have the indicated large temperature range (254 to 313§C) given above.

Statistical calculations could not be carried out for some of the groups because there were no data in them. For other groups, the mean and standard deviations are shown as data set E in Table 1. The data show that there is no systematic difference in the D pickup rates shown by the QM and DM materials. In some groups the QM material has superior resistance to D pickup and in other groups the DM material is superior.

4.3.3. Transverse Tensile Properties

The tensile properties were measured at 250§C in samples machined (and not flattened) from the transverse direction in the tubes. The results, summarized as data set F in Table 1, show that the QM tubes are slightly superior to the DM tubes, but the differences are small.

4.3.4. Delayed Hydride Crack Growth Rates (DHCV) at 130§C

Delayed hydride cracking is a slow stable crack growth mechanism that requires the presence at a flaw tip of a sufficiently large tensile stress and hydrides. Thus, the maximum temperature at which tests can be carried out depends on the hydrogen equivalent concentration and for many tests the selected temperature is 130°C. A database containing results from 100 delayed hydride crack growth rate (DHCV) tests carried out at 130°C on material from pressure tubes removed during LSFCR was examined for an effect of the ingot melting practice on the DHCV results.

The results obtained are summarized as data set G in Table 1. They indicate that there is little difference in the DHCV results for the irradiated pressure material removed during LSFCR, with the small difference in favor of the QM material.

5.0 OTHER MEASUREMENTS

The axial elongation rate data summarized as data sets B and C in Table 1 show that there is no systematic difference in the elongation rates for QM and DM material. For data set B information on the actual amounts of recycled material in the ingots was available and the elongation data were examined for differences that could be attributed to the amount of recycled material in the ingots. The elongation data for the pressure tubes was sorted by ingot number and the average elongation rate calculated for the tubes from each ingot (called ingot average elongation rate). The ingot average elongation rate was then plotted against the amount of recycled material in each ingot. The results in Figure 7 show that there is no systematic dependence of the ingot average elongation rate on the amount of recycled material in the ingots.

6.0. DISCUSSION

Measured data confirm that pressure tubes made from QM material have superior fracture toughness properties to those made from DM material. The results from measurements made on pressure tubes before, during and after service show that their other properties were not dependent on the number of times that the ingots were melted, i.e., on whether the ingots were QM or DM.

The reason for the improved fracture toughness in the QM material is attributed to the reduction in the concentration of chlorine (Cl). It was shown that the fracture toughness was affected by the presence of stringer-like features in the microstructure (Davies et al., 1994), with the toughness increasing with a reduction in the number of the stringers and in their size. The stringers were not present when the material had the low chlorine concentrations that were achieved when the ingots were melted 4 times (QM). It was also shown that the stringers were chlorine-rich.

Measurements of the concentrations of the other elements in QM material show that they were within the range of concentrations seen in other Zr-2.5Nb ingots. Thus the behavior of the QM material during forging, extrusion and cold drawing would have been within the range seen in all of the ingots. Then the final microstructures (except for the Cl-rich stringers) would have been similar in all of the materials.

Since the mechanical properties and corrosion behaviour of pressure tube materials depend on the microstructures, it is not surprising that the mechanical properties (in- and out-reactor) and the corrosion and D pickup behavior were found to be similar in the QM and DM materials when compared under similar conditions.

Note that the superior fracture toughness of the QM tubes is associated with low concentrations of chlorine. It is possible to achieve low chlorine concentrations and superior fracture toughness values by the use of other methods not requiring QM, e.g. starting with material already low in chlorine.

7.0. ACKNOWLEDGEMENTS

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8.0 REFERENCES

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Davies, P.H., R.R. Hosbons, M. Griffiths and C.K. Chow, "Correlation Between Irradiated and Unirradiated Fracture Toughness of Zr-2.5Nb Pressure Tubes", Zirconium in the Nuclear Industry, 10th International Symposium, 1994, ASTM STP 1245, pp.135-167.

Data Set	Property Measured	In/Out Reactor	QM Mean	QM StdDev	QM Count	DM Mean	DM StdDev	DM Count
A	UTS, Front	Mfg	518.8	15.2	230	511.9	14.5	1690
A	YS, Front	Mfg	394.1	26.2	230	392.0	22.7	1690
A	El, Front	Mfg	15.1	1.9	230	14.6	1.6	1690
A	Corr Wt gain	Mfg	25.1	2.6	230	24.5	1.9	1690
B	Axial elongation rate	In	6.43	0.76	80	6.99	0.79	1350
C	Axial elongation rate	In	6.40	0.71	177	6.49	0.76	603
D	ID oxide, Z1, 248-270C	Post	5.7	0.4	31	5.7	0.5	140
D	ID oxide, Z1, 270-291C	Post	10.4	3.3	44	9.8	3.0	217
D	ID oxide, Z2, 248-270C	Post	5.8	0.6	18	5.7	0.4	103
D	ID oxide, Z2, 270-291C	Post	9.4	2.7	51	9.1	2.4	225
D	ID oxide, Z3, 248-270C	Post	5.6	0.1	8	5.7	0.4	24
D	ID oxide, Z3, 270-291C	Post	6.9	1.3	12	7.9	1.6	51
E	D rate, Z1, 254-283C	In/Post	0.71	0.42	24	0.93	0.48	244
E	D rate, Z1, 284-313C	In/Post	1.99	0.73	58	1.69	0.52	375
E	D rate, Z2, 254-283C	In/Post	0.44	0.31	5	0.76	0.34	44
E	D rate, Z2, 284-313C	In/Post	1.74	0.5	12	1.55	0.64	79
E	D rate, Z3, 254-283C	In/Post	-	-	0	0.60	0.34	32
E	D rate, Z3. 284-313C	In/Post	-	-	0	1.01	0.41	19
F	Trans UTS, 250C	Post	858.6	45.3	25	847.4	48.5	66
F	Trans YS, 250C	Post	863.7	45.3	31	857.5	41.9	79
F	Trans RA, 250C	Post	30	7.3	31	28.7	6.7	79
G	DHCV 130C	Post	6.9	1.3	12	7.9	1.6	51

Table 1
Data showing the effect of double melting (DM) and quadruple melting (QM) on the properties of cold worked pressure tubes measured during manufacture (Mfg), or in-reactor (In) or after removal from service (Post). The letters in column 1 refer to different sets of data and the properties measured are indicated in column 2 (ID = Inside Surface, Z1, Z2 and Z3 refer to the different power zones). The mean and standard deviation values are given together with the number of data examined. The units are arbitrary, but are the same in the DM and QM columns.

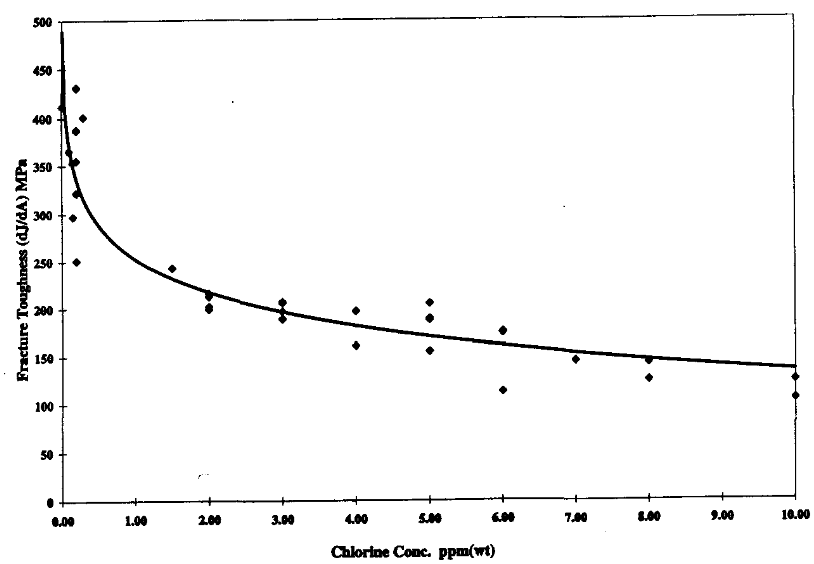


Figure 1
Graph to show the effect of chlorine concentration on the fracture toughness (dJ/da) of Zr-2.5Nb pressure tube material containing less than 10 ppm phosphorus at 250°C.

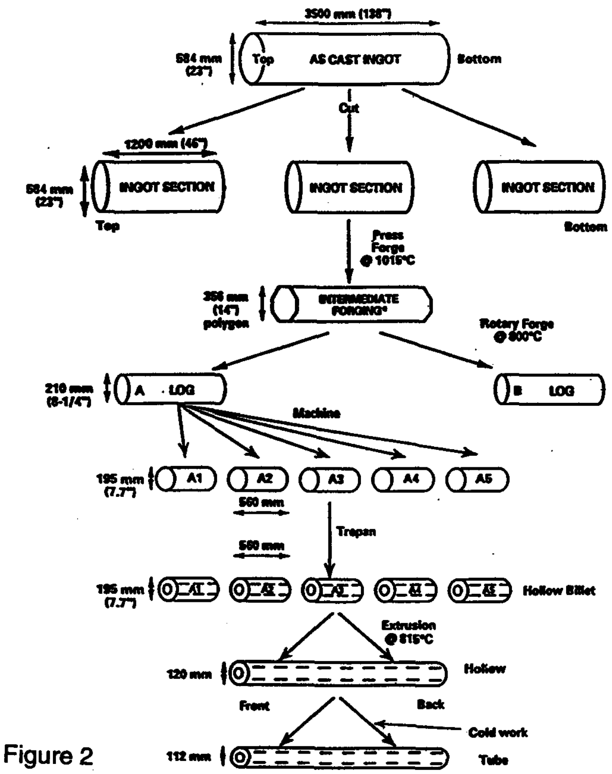


Figure 2

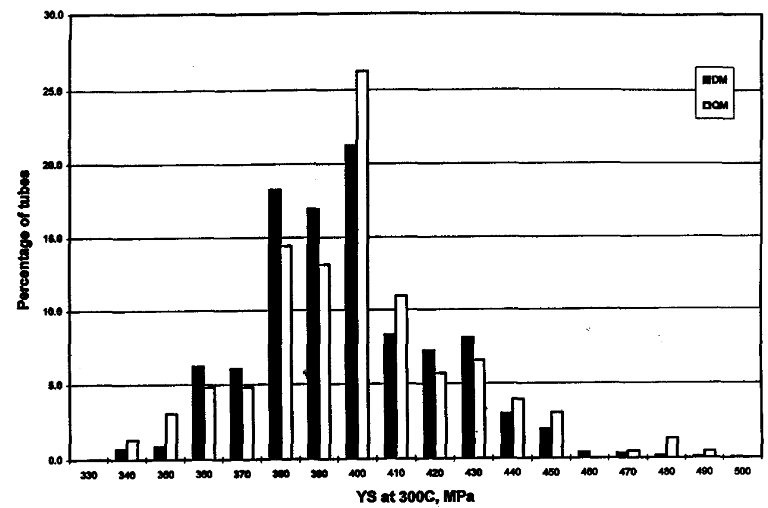


Figure 3

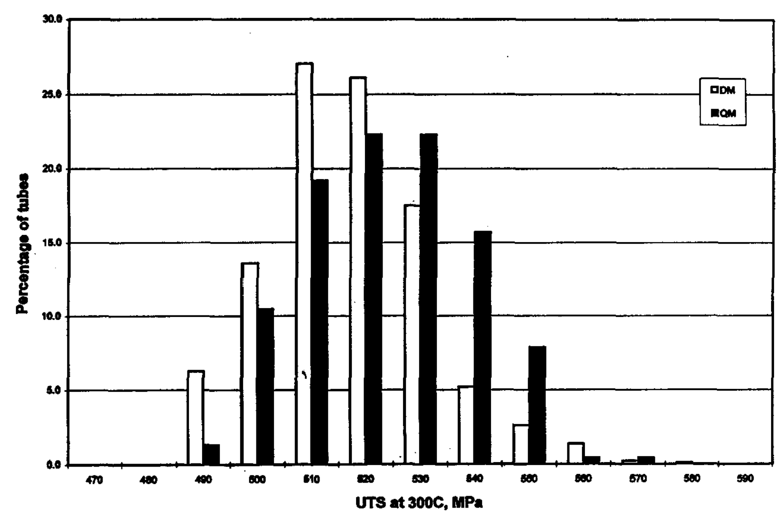
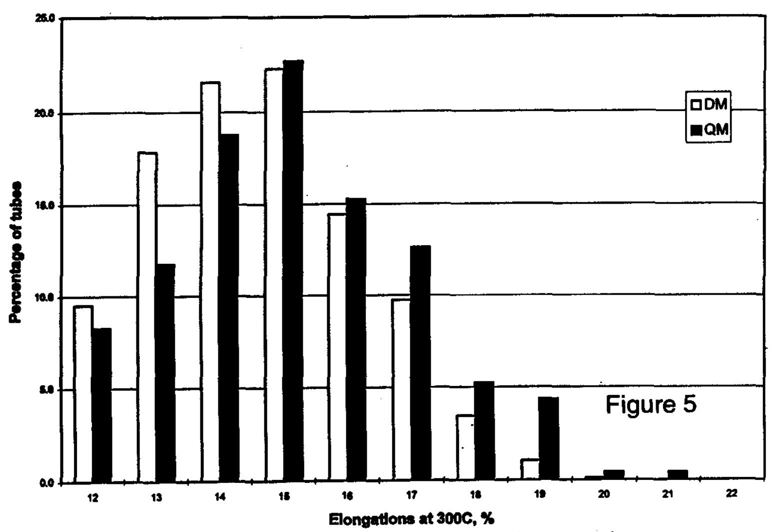


Figure 4

Figure 2
Sketch to show the principal stages in the processing of cold worked Zr-2.5Nb pressure tubes for CANDU fuel channels

Figure 3
Histogram to show the effect of ingot melting practice on the distribution of the yield strength (YS) in the front end of Zr-2.5Nb pressure tubes at 300°C.

Figure 4
Histogram to show the effect of ingot melting practice on the distribution of the ultimate tensile strength (UTS) in the front end of Zr-2.5Nb pressure tubes at 300°C.



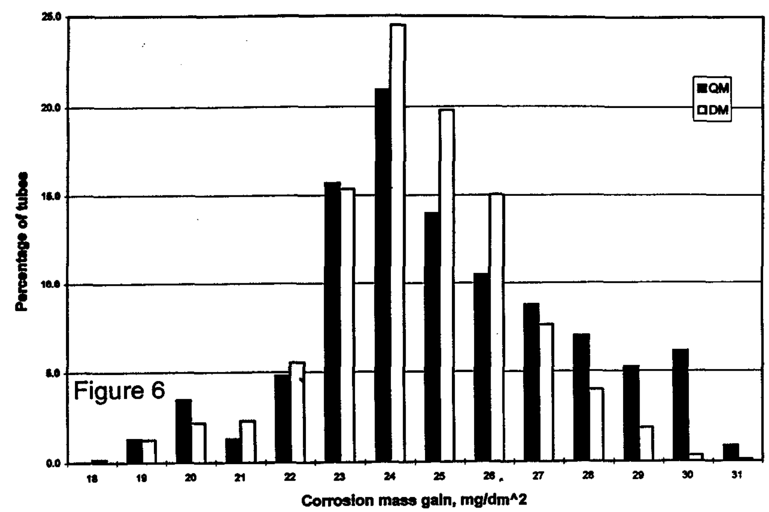


Figure 5
Histogram to show the effect of ingot melting practice on the distribution of the elongation in the front end of Zr-2.5Nb pressure tubes at 300°C.

Figure 6
Histogram to show the effect of ingot melting practice on the distribution of the corrosion weight gains in ASTM G2 autoclave corrosion tests by Zr-2.5Nb pressure tubes at 400°C.

Figure 7
Data showing the effect of the amount of recycled material in an ingot on the ingot average axial elongation rate in reactor for the tubes made from the ingot. The ingot average axial elongation rate is the average rate for all of the tubes made from the ingot.

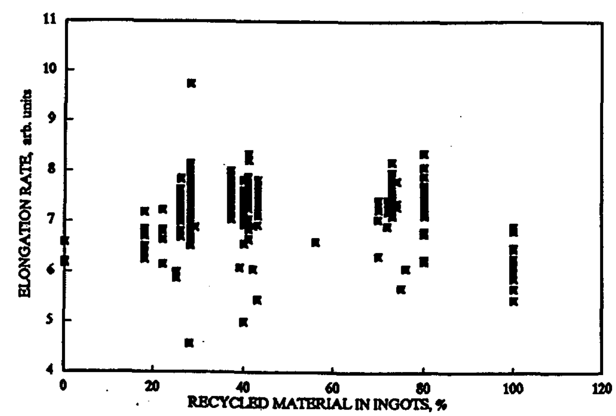


Figure 7