Proceedings of the 15th International Symposium on the Packaging and Transportation of Radioactive Materials
PATRAM 2007
October 21-26, 2007, Miami, Florida, USA

EXPERIENCE WITH QUALIFICATION OF METAL MATRIX COMPOSITES USED AS FIXED NEUTRON ABSORBERS

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ABSTRACT

Since Transnuclear first introduced the use of boron carbide / aluminum metal matrix composites (MMCs) in the TN-68 storage and transport cask, other cask designers have begun to use these materials, and new suppliers have entered the market. The interest of the US regulator in how these materials are qualified for use is demonstrated by the ASTM work item WK936 which was initiated by US NRC staff members.

MMCs lack a long history of large-scale manufacturing, and there are no widely-accepted standard specifications for manufacturing and inspecting them. Thus, it becomes necessary to develop methods for demonstrating that the material is suitable for its intended use, that it will perform in its working environment for the design lifetime, and that the manufacturing methods will be consistent.

Initial efforts at materials qualification, the qualification of Boralyn® by Transnuclear (the designer), and the qualification of Metamic® by the Reynolds Corp. (the supplier) were quite extensive and correspondingly expensive. Because changes to manufacturing processes might require re-testing, and because that re-testing could be prohibitively expensive, such qualification programs could become an impediment to product development. Therefore, for its current license applications, Transnuclear has developed a more focused approach to MMC qualification along the lines of the WK936 work item. This approach requires collaboration of the supplier and the designer – the supplier cannot know all of the design requirements for the material, and the designer cannot know all of the appropriate controls to supply a consistent product. The first such license application to be approved is the NUHOMS® HD, USNRC CoC 1030. This paper examines the concepts behind this approach, and the practical implementation experience qualifying Alcan MMC for use in the NUHOMS® HD canister.

INTRODUCTION

Used nuclear fuel storage systems use neutron absorbing material (also called "poison") to maintain criticality control during storage. Neutron absorbing materials used in Transnuclear's products are typically in plate form and comprised of an aluminum or aluminum alloy matrix in which boron is dispersed in the form of B_4C, AlB_2, or TiB_2 using natural or isotopically enriched boron. Isotopic ^{10}B is the only significant source for neutron absorption in these materials.

Various products exist on the market from which storage system designers may choose. With variation of products comes variation of material properties, which in turn, may influence the performance of the storage system. Neutron absorbing materials are typically classified with the highest category of safety significance which also increases the scrutiny of the material. Extensive material qualification programs are implemented to define the performance properties of the material. These qualification programs are expensive, and when changes or even enhancements occur in the product (e.g. material chemistries, manufacturing techniques, etc), re-testing is required. This impedes the material supplier from pursuing product development and can create a bottleneck inhibiting used fuel storage designers from bringing improved materials to the market.

Once qualification programs are completed the expected material performance is defined. The designer reduces the material performance in analytical models to provide design margin. Oftentimes, the use of new or changes to existing neutron absorbers requires the designer to seek approval from the Nuclear Regulatory Commission adding an additional review cycle. Once the use of the material is approved, acceptance testing requirements for production material are defined to ensure material reliability and consistency in production.

MMC DEVELOPMENT

From August 2006 to present, Transnuclear, Inc. is working in conjunction with Ceradyne Canada and Alcan on a type of neutron absorbing material generically called Metal Matrix Composite (MMC). Revision 0 to the NUHOMS® HD Final Safety Analysis Report for Certificate of Compliance 1030, Amendment 0, refers to MMC as a composite of fine boron carbide particles in an aluminum or aluminum alloy matrix. MMC is produced by direct chill casting, permanent mold casting, powder metallurgy, or thermal spray techniques. It is a low-porosity product, with a metallurgically bonded matrix. The boron carbide content can not exceed 40% by volume for this license.

The NUHOMS® HD licensing basis defines a focused approach for qualifying MMC which follows the development of the draft ASTM C 1671-07, "Qualification and Acceptance of Boron Based Metallic Neutron Absorbers for Nuclear Criticality for Dry Cask Storage Systems and Transportation Package", work item WK936. This approach requires TN and the MMC supplier to develop, in unison, a material that meets TN's unique design requirements and also generic requirements for proper classification as an MMC. The long term advantage for TN and the MMC supplier is the ability to evaluate the important aspects of production and establish minimized re-qualification requirements if the production process is changed. These important aspects are referred to as Key Process Controls and are maintained in a living document that TN and the MMC supplier use as the basis for the development and procurement of that supplier's MMC. As the MMC supplier advances material performance, such as increased boron loading, or implements cost savings, such as relaxed feed material specifications, re-qualification steps are outlined for a cost-efficient verification of material performance that can be realized between different projects.

For initial qualification of an MMC, the following material characteristics are verified:

- Boron Uniformity (verification by areal density testing)
- Thermal Conductivity
- Density
- Porosity
- Mechanical Properties
- Corrosion Resistance (Optional for MMC using Al type 1100 matrix)
- Thermal Durability (Optional for MMC using Al type 1100 matrix)

It is important to understand that the only characteristics of MMC that are credited in TN's design analyses are thermal conductivity and ^{10}B areal density. No structural credit is taken, the sole exception being that the material is expected to act in compression between the stainless steel fuel compartments and basket components. The remaining material characteristics of MMC are established values that comprise the generic material performance and hence classification as an MMC. Conformance with the material performance requirements must be met during development and maintained during evolution of the MMC. After initial qualification, only the material characteristics that are credited in analysis are verified for each lot of received product, specifically:

- Areal density, verified at 95% confidence and 95% probability
- Thermal conductivity

The first project that procured MMC under this new approach was the 32PTH Dry Shielded Canister (DSC) that is licensed under the Certificate of Compliance No. 1030, Amendment 0, for the NUHOMS® HD System. A material qualification effort was started in the fourth quarter of 2006 with completion in the middle of 2007. The 32PTH basket design required:

- ≥ 20 mg ^{10}B/cm^2, areal density
- 145 w/mK, thermal conductivity

To meet the areal density requirements, the supplier selected a nominal 16% B_4C content with a nominal plate thickness of 0.170 inch (4.3 mm), which correlates to target areal density of 24.5 mg ^{10}B/cm^2. The ^{10}B margin over the minimal design requirement accounts for the statistical analysis used for demonstrating 95% confidence and 95% probability.

DISCUSSION OF QUALIFICATION RESULTS:

Boron Uniformity

MMC suppliers are permitted to use small scale production lots for material qualification. This to minimize the amount of potentially scrapped material, provided that the supplier can justify acceptable differences between a qualification lot and full scale production lot.

Ceradyne and Alcan provided qualification coupons from a full scale production lot, defined as a single 5 ton casting of material, typically yielding 16 logs that are each cut into eight or nine billets. For the MMC plate sizes of the 32PTH, a single billet can produce four plates. To systematically distribute the location of the samples through the casting, two coupons were taken from each billet of material. The boron uniformity of the qualification lot was accepted, as follows.

Units: mg ^{10}B/cm^2

23.0	MEAN
2.30	10% of MEAN
0.37	1 standard deviation

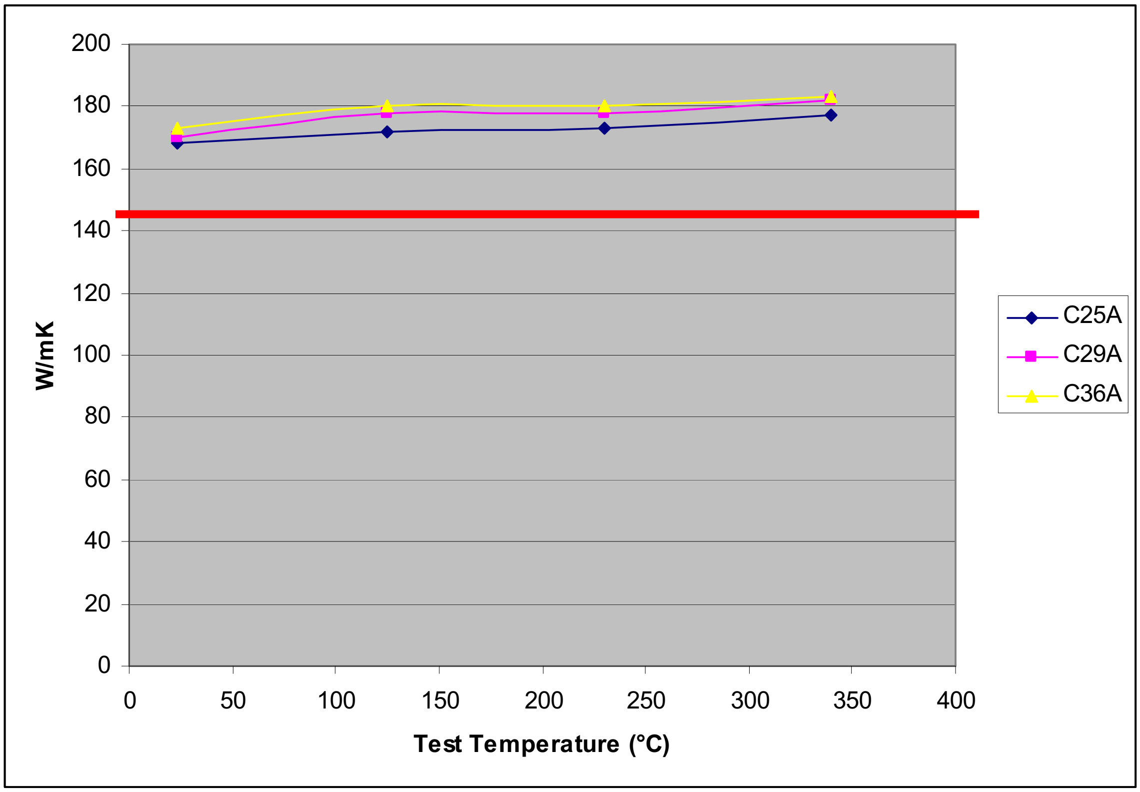
Thermal Conductivity

Thermal conductivity was tested in accordance with ASTM E-1225, "Standard Test Method for Thermal Conductivity of Solids by Means of the Guarded-Comparative-Longitudinal Heat Flow Technique." A minimum thermal conductivity of 145 W/m-K is used in the thermal models for the 32PTH DSC. The thermal conductivity is also measured at elevated temperatures to ensure design requirements are met through temperature transients.

As shown below, each coupon at each test temperature met the minimum 145 W/m-K.

Sample ID	**Nominal Temperature (^{o}C)**	**23**	**125**	**230**	**340**
C25A	Tested Temperature (^{o}C)	23	126	229	339
	Conductivity (W/m-K)	168	172	173	177
C29A	Tested Temperature (^{o}C)	24	128	231	341
	Conductivity (W/m-K)	170	178	178	182
C36A	Tested Temperature (^{o}C)	23	126	230	340
	Conductivity (W/m-K)	173	180	180	183

The figure below graphs the minimum design requirement, represented by a red line, against the actual test results.



Mechanical Properties

No structural credit is taken for MMC in the 32PTH. The acceptance criteria are set reasonably low with respect to published values of tempered aluminum, and is primarily used as spot-check that the casting process, boron-rich ingredients, or final forming processes haven't created a low strength or brittle material.

	Testing Temperature	**Min Yield Strength (ksi)**	**Min Ultimate Strength (ksi)**	**Min Elongation in 2 inch (%)**	**Evaluation**
Acceptance Criteria	Room	5	1.5	0.5	
Sample ID					
T29A	Room	21.5	23.7	5.5	Acceptable
T25A	Room	20.7	22.2	4.0	Acceptable
T36A	Room	21.2	23.5	4.0	Acceptable

Density

For Ceradyne and Alcan's neutron absorbing material to be appropriately categorized as an MMC, the material needed to be close to fully dense, which was quantified as >98.5% of theoretical density. This property in particular was problematic during the material qualification.

Measuring the actual density of the material is simpler than determining what value should be defined as theoretical density. The chemical balance between castings could potentially vary enough that the no single theoretical density could be used for each casting. It also important to note that defining the theoretical density was truly not the intent of the qualification step. The intent was to ensure that the manufacturing process yielded a final product that was not porous, and 98.5% of theoretical density was an attempt to create a quantifiable expression.

From the production records of the qualification heat, the mass of aluminum, boron carbide, and other significant alloying ingredients, i.e., titanium, were used to calculate a theoretical density, which was only representative of the qualification heat. The resulting theoretical density is given below.

$$\rho_{MMC} = \rho_{Al}\left(\frac{mass_{Al}}{mass_{MMC}}\right) + \rho_{B4C}\left(\frac{mass_{B4C}}{mass_{total}}\right) + \rho_{Ti}\left(\frac{mass_{Ti}}{mass_{Total}}\right)$$

$$\rho_{MMC} = 2.6920\ (\mathrm{g/cm^3})$$

The next step taken was to measure the actual density of the qualification heat. The test method selected was ASTM B311, "Test Method for Density Determination of Powder Metallurgy (P/M) Materials Containing less than Two Percent Porosity." A larger than originally anticipated sample of three coupons was taken to ensure detection of any fluctuation of density through the casting. Fifty-one coupons were selected from various locations of the casting.

The test results showed a final product with exceptional uniformity, an average density of 2.6886 (g/cm^3) with standard deviation of 0.0027. With a standard deviation of > 0.1% of the average value, the results were considered sufficiently accurate and repeatable.

To ensure reliability of the test equipment used, the laboratory validated their test method by measuring the density of a sample of high purity aluminum (99.9997 wt. %) against the published density of pure aluminum, 2.70 g/cm^3. After 5 measurements an average density of 2.7003 (g/cm^3) was calculated, which represents a negligible 0.011% deviation from theoretical.

In summary, the MMC product was accepted as a near completely dense product the quantified comparison is provided below.

Actual Density (g/cm^3)	**Theoretical Density (g/cm^3)**	**%**	**% Acceptance Criteria**
2.6886	2.6920	99.87	>98.5

In addition to density testing in accordance with ASTM B311, eight coupons were polished and etched for microscopic examination of sub-surface porosity. At sufficient magnification, imagery analysis of the microstructure was used to quantify detectable voids. The average porosity of 0.078% was calculated with a standard deviation of 0.022, which corresponds to a 99.92% dense material.

Porosity

Surface porosity was tested in accordance with ASTM B-328, “Standard Test Method for Density, Oil Content, and Interconnected Porosity of Sintered Metal Structural Parts and Oil-Impregnated Bearings.”

	Max Porosity (%)	**Evaluation**
Acceptance Criteria	<0 .5	
Sample ID		
P29A	0.082	Acceptable
P25A	0.082	Acceptable
P36A	0.065	Acceptable

These results coincide with the density results, as substantial surface porosity would only be expected if the density results could not be accepted.

Corrosion Resistance

Two samples from the qualification heat were subjected to separate water baths that simulate spent fuel pool water conditions during spent fuel loading operations. The water chemistries included 2000 ppm borated water and de-mineralized water, for a pressurized water reactor and a boiling water reactor, respectively. The performances of the MMC samples were compared against two samples of 99% pure aluminum that were subjected to the same water baths. By demonstrating acceptability in both chemistries, the MMC can be qualified for both reactor types.

The testing lasted a minimum of 96 hours with a water temperature of 190°F. The performance of the MMC samples was reviewed against the criteria listed below.

- General corrosion, as measured by thickness increase, shall not be greater than that of the aluminum 1100 coupon.
- Slightly more pitting corrosion than the aluminum 1100 coupon is acceptable; if the number of pitting sites or the size of the pits is more than twice that of aluminum 1100, further evaluation will be required.

Results of Thickness Measurements

Sample ID	Thickness (inch)	Post-Test Thickness (inch)	Difference	Conclusion
51A	0.1694	0.1693	Negligible	Acceptable
52A	0.1704	0.1706	Negligible	Acceptable
Aluminum 1100 Sample ID				
290526-152 TN1	0.3197	0.3200	Negligible	N/A
290526-152 TN2	0.3206	0.3205	Negligible	N/A

No off-gassing, which presumably would be hydrogen, was observed during the test.

Microscopic examination of the MMC samples showed that boron carbide particles were not present at the surface. Cold rolling smears the softer aluminum across the embedded boron carbide particles, thus creating a rough and pitted surface that results in indeterminate micrographs before and after the water bath. To quantify the loss of material, most importantly the boron carbide, 1.2µm polycarbonate membrane filters were used to isolate any loose particles that came free during immersion. No boron carbides were detected in the filters, and through energy-dispersive x-ray mapping, only aluminum rich by-products that were shed during the reaction/corrosion between the aluminum and water baths were detected in the filters.

Discoloration of the MMC and aluminum samples occurred during the first 24 hours of the borated water bath, with the MMC sample demonstrating the darker discoloration. This was believed to be behavior similar to fresh aluminum surfaces in contact with atmospheric oxygen which develop a thin oxide coating quickly and virtually stop corroding. This is also supported by the MMC sample in the borated bath resulting in a weight increase of 0.3 gram, and the collection filter with a weight increase of 0.004 gram, whereas the MMC sample in the de-mineralized bath had no discoloration, resulting in a weight increase of 0.005 gram, and the filter gaining 0.0002 gram. The weight increase and discoloration of the MMC sample are concluded to be similar to a short-lived passivation brought on by the aluminum of the MMC reacting with the borated water. The surface reaction is acceptable based on no boron-carbide particles detected in the filters, negligible difference in the thickness measurement, and the aluminum sample demonstrating less darkening passivation phenomena.

In summary, the MMC samples reported no greater general corrosion than that of the aluminum samples and negligible differences in thickness measurements were reported. The surface reactions in the borated water bath, evident by discoloration, were acceptable and demonstrated by both the MMC and aluminum samples. The MMC demonstrated acceptable corrosion resistance properties for borated spent fuel pools of a pressurized water reactor and non-borated spent fuel pools of a boiling water reactor.

Thermal Durability

The test setup for thermal durability involved placing three tensile specimens in an argon filled mesh bag then placed in a furnace at 825 – 840 °F for a minimum of 30 days. The lengths of the specimens were measured before and after the heat treatment, and found acceptable, i.e., less than ±0.1% change. The specimens were found acceptable, as follows.

Coupon ID	Length Before Heat Treatment	Length After Heat Treatment	% Length Change
T25B	5.9535	5.9535	0
T54B	5.9375	5.9365	- 0.02
T35B	5.9695	5.9685	- 0.02

After length verification, the samples were visually examined to determine if mechanical damage such as cracks or blisters had occurred. None were found, but a laminar defect was discovered along the edge of sample T35B. Such laminar defects acting parallel in the direction of rolling have negligible impact on the mechanical properties of the material and no effect on the neutron absorption function[1]. Finally, the three samples were tensile tested and passed the acceptance criteria for mechanical properties.

	Testing Temperature	Min Yield Strength (ksi)	Min Ultimate Strength (ksi)	Min Elongation in 2 inch (%)	Evaluation
Acceptance Criteria	Room	5	1.5	0.5	
Sample ID					
T25B	Room	18.8	8.6	16	Acceptable
T54B	Room	18.8	8.6	20	Acceptable
T35B	Room	19.0	9.0	15	Acceptable

ACCEPTANCE TESTING

Areal Density

The objective of the neutron transmission acceptance testing is to show that each heat has an areal density greater than 20 mg $^{10}B/cm^2$ at the 95% probability and 95% confidence, or better.

The method of statistical analysis chosen is a "One-Sided Tolerance Limit" based on measured areal density divided by measured thickness to yield the volume density at the location of each coupon. The lower side tolerance limit of ^{10}B is then determined, defined as the mean value of ^{10}B volume density for the heat, less K times the standard deviation, where K is the one-sided tolerance limit factor for a normal distribution with 95% probability and 95% confidence. Finally, the 20 mg $^{10}B/cm^2$ is divided by the lower tolerance limit of ^{10}B volume density to arrive at the minimum plate thickness that would provide the specified areal density. The factor K is tabulated for normal distributions, if the test data are not normal, a different method should be used. In the case discussed here, the data tested normal.

This approach not only demonstrates the acceptability of the final product, but presents available margin in terms of plate thickness, which can be used for additional means, e.g. accepting non-conforming plate thicknesses. The plates were manufactured with a plate thickness of 0.170 ± 0.005", therefore if t_m is shown to be less than 0.165", then the material from the applicable heat is acceptable. The results are summarized in Table 1.

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[1] These laminar defects were observed in other specimens not subjected to thermal durability testing, and are believed to be the result of inclusions in the billet, not high temperature exposure.

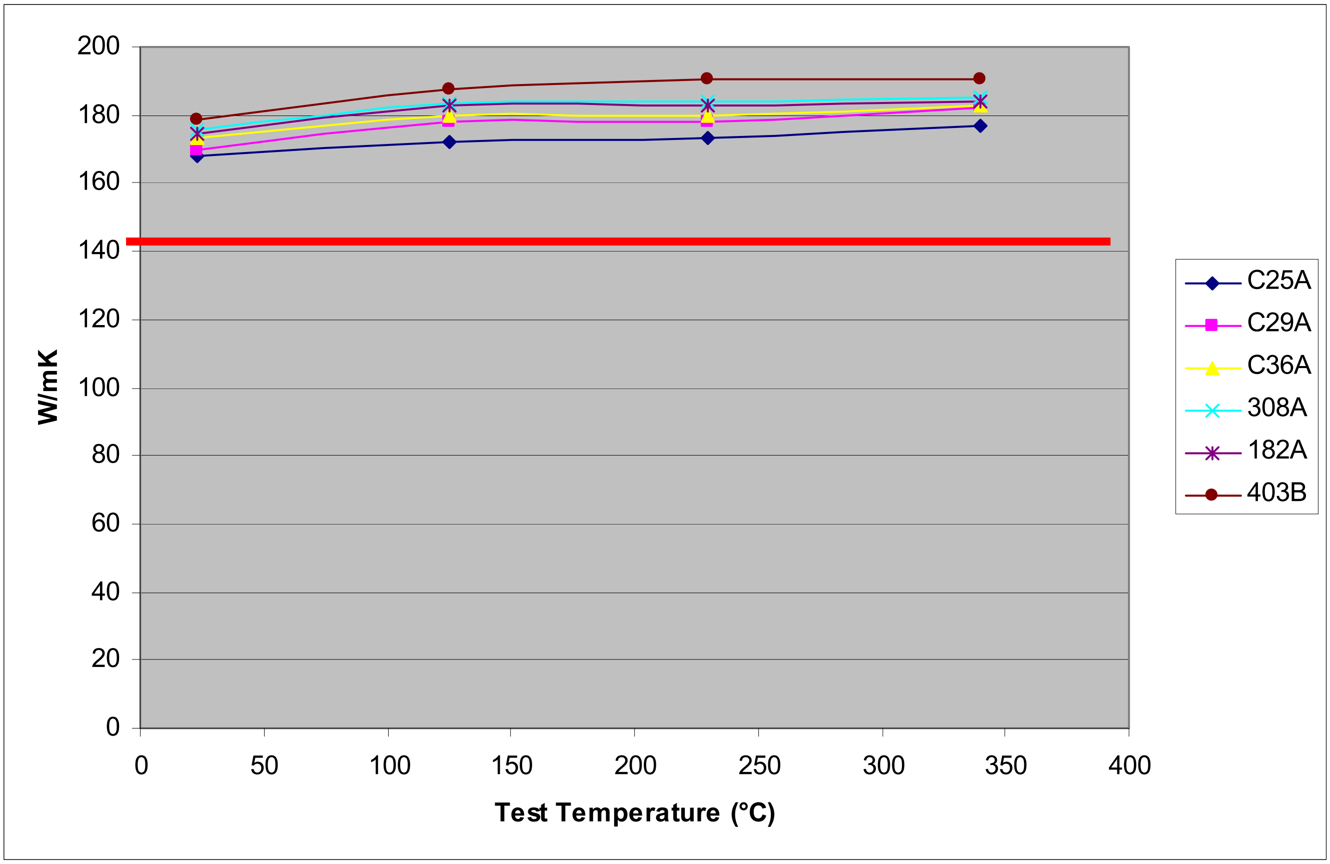
Table 1 – Summary of Statistical Analysis

Heat	X_{MEAN}	K	s	X_L	t_m
6654	133.932	1.818336	1.721220	130.8	0.153”
6667	135.464	1.830453	1.426551	132.9	0.151”
6668	138.265	1.810418	1.998814	134.6	0.149”
6672	134.567	1.811161	1.184519	132.4	0.151”

Thermal Conductivity

The data below represent the thermal conductivity of the first four castings used for production; all results are acceptable. It is also noted that the trend of rising thermal conductivity with test temperature is seen in all castings and the data conforms to expectations, based on the published thermal conductivity values and volume percentages of the aluminum, boron carbide, and additional alloying ingredients.

Sample ID	**Nominal Temperature (^oC)**	**23**	**125**	**230**	**340**
C25A	Tested Temperature (^oC)	23	126	229	339
	Conductivity (W/m-K)	168	172	173	177
C29A	Tested Temperature (^oC)	24	128	231	341
	Conductivity (W/m-K)	170	178	178	182
C36A	Tested Temperature (^oC)	23	126	230	340
	Conductivity (W/m-K)	173	180	180	183
308A	Tested Temperature (^oC)	23	127	230	340
	Conductivity (W/m-K)	176	183	184	185
182A	Tested Temperature (^oC)	23	127	230	340
	Conductivity (W/m-K)	175	183	183	184
403B	Tested Temperature (^oC)	23	127	230	340
	Conductivity (W/m-K)	179	188	190	190



CONCLUSIONS

1) Material Delivery Control
To accept the areal density of a casting, all material from that heat must be processed, tested, and used to complete the statistical analysis. The risk is that the canister fabricator will receive material that has not yet been shown to meet the minimum areal density requirements. This puts any spent fuel storage systems built with these poison plates at-risk until all material has been tested and accepted.

TN now requires its suppliers to develop material delivery control plans that will permit TN to completely test and accept a heat, before any poison plates from that heat are used in fabrication.

2) Understanding Your Thermal Analysis
Various testing standards exist for measuring thermal conductivity. Prior to selecting which standards shall be used, discuss with the thermal analyst which test method most accurately represents how the material behaves in the model, e.g., thru-thickness conductivity vs. longitudinal conductivity.

3) Invest in a Preliminary Manufacturing and Testing Campaign
A small processing campaign is always a good idea for first time poison plate production. This will allow the poison plate supplier to fine tune items before large scale production begins. Important items to evaluate include adequate billet size, rolling parameters, understanding surface finish requirements, and shearing capabilities within required

tolerances. Working through these items before your campaign will minimize the amount of non-conforming rejected plates, and schedule delays.

A mini-campaign will also allow the spent fuel storage system designer to perform preliminary tests to make a commercial assessment of first time materials and begin any necessary evaluations if it is anticipated that material will not meet minimum design requirements

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4) Not all Plate Thicknesses Shear the Same
   TN placed a follow-up order for the same MMC composition with a final plate thickness almost double of the original order. During final shearing the material unexpectedly bowed out of tolerance with TN flatness requirements. The plates were ultimately reworked by furnace flattening, but caused a material delivery delay and unexpected expense to the supplier. This is another item that could have been identified and resolved in a mini-campaign.

5) Resolving the Problems Caused by Byproducts
   Intermetallic compounds in the heat would come to the surface during plate rolling, resulting in surface defects that require reworking and re-inspection and often rejected material. Alcan was able to refine the dross filter controls during casting and pouring, removing these byproducts. Plates from subsequent rolling campaigns had improved surface finishes and dramatically reduced surface defects, which saved time and money for all parties involved.

6) Exceed the Minimum Sampling Requirements
   Always order more coupons than needed, in case they are misplaced by a laboratory or lost in transportation. There could also be a need to withdraw coupons from testing, when material conditions could cause false failures, e.g., unacceptable surface conditions, below minimum thickness, and edge cracking. Coupons should be subject to areal density verification if they pass the same dimensional and visual acceptance criteria as the finished plate.