ARCHIVES of FOUNDRY ENGINEERING

ISSN (1897-3310)
Volume 16
Issue 3/2016

5 – 10

1/3

Published quarterly as the organ of the Foundry Commission of the Polish Academy of Sciences

Identification and Quantification of Gases Releasing From Furan No Bake Binder

S.G. Acharya [a]*, J.A. Vadher [b], P.V. Kanjariya [c]
[a] Department of Mechanical Engg., S.V.I.T Vasad , Vadodara, Gujarat, India
Ph.D Scholar, School of Engineering, R. K. University, Rajkot, Gujarat, India
[b] Department of Mechanical Engg., Govt. Egg. College, Palanpur, Gujarat, India
[c] General Department, A.I.T.S Rajkot, Gujarat, India
*Corresponding author. E-mail address: shailee.acharya@gmail.com

Received 03.01.2016; accepted in revised form 14.02.2016

Abstract

Sand samples with furan binder were prepared using Sand, Furfuryl Alcohol and Toluene Sulfonic Acid with ratio 100:0.85:0.30. To identify and quantify gases releasing from furan binder various studies like FTIR, TGA and GC-MS were carried out. After analyzing our materials using above mentioned characterizations the chemical formula of the Resin and Binder and amount of gases releasing from composition were confirmed. After studying various reports on pyrolysis process of furan binder calculation of the % of various gases emitting during pyrolysis process of furan was carried out. Sample of gas collected from mold was analyzed using GC-MS. Based on GC-MS measurement various gases emitting from furan sand mold were identified and their amount were calculate and compared with the international standers of permissible gas emission limits in a foundry. The purpose of this paper is to assist foundries in pollution prevention by devising clean technologies which maintain or improve the quality of ambient surrounding. This paper aimed at minimization of pollution of air by using various techniques.

Keywords: Furan, GC-MS, FTIR, Furan no bake, Binder, Pyrolysis

1. Introduction

Metal casting industries has been described as “The most direct and shortest route from component design to production”. [1] Almost any ferrous and non ferrous metal that can be melted can also be cast, and the design of the casting can be very flexible. This flexibility allows the foundry industry to produce simple or complex components of enormous variety, whether they are produced once as a prototype or thousands of times for use in a manufactured product. It is not surprising that for 90% of all manufactured goods andall machinery for manufacturing are prepared through metal forming technique. [1] The present and future adverse effect of this foundry process, their damage to our environment and to the earth’s ecosystem and ultimately their effect on the quality of human life are by now well familiarto the world. Casting plays valuable role in effect of water and air pollution, acid rain, ozone exhaustion, the green house effect, hazardous waste, and global warming. [2]

Due to casting foundry is being required to seek for energy-saving, environment friendly and more efficient casting methods. No-bake binders have shown aggression to this problem by addressing the casting quality, efficiency and environmental attributes. The no-bake furan resin bonded sand can be achieved at room temperature, is characterized by high strength, high dimensional accuracy, fast hardening rate, high production efficiency and low labor intensity as well as abundant source of raw material and simple manufacturing process. [2] Therefore, furan resin is widely used in casting. Nowadays due to environmental and energy benefits our Indian foundries are also

looking for such sustainable solution to remain viable. In our country No-bake furan binder system is adopted by few industries. One of such industry, I have visited is Krislur Castomech Pvt. Ltd. Founded in 1980, it is one of the most promising and reputed industry in terms of quality of sand casting. It is situated at GIDC Bhavnagar, Gujarat, India. The Industry has been certified by ISO 9001:2008. The main emphasis of the industry is production of motor body and its allied parts.

1.1 Furan No Bake Binder System

Heat activated, no bake and cold box are three main classes of binder systems. [3] In this paper we studied the thermal degradation of Furan in Furan no back binder system. Furan No-bake processes is binder system for producing cores, core moulds or plain moulds. Furan resin is made up of furfuryl alcohol and its most important application is foundry. No-Bake furan mould is used in casting all kind of cast steel, cast iron, non-ferrous metal casting. The binder may be cured with a gas or a liquid catalyst. This process forms hard, rigid cores and moulds, giving the casting good dimensional tolerances. The sand in a no-bake mould is mixed with a liquid resin and hardens at room temperature. The no bake binders are either acid catalyzed or ester cured. [4] Heat is not required in the process. The operating temperatures for this process range from 24 to 30 ºC. The sand, binder, and catalyst are continuously mixed and blown into the core box. The amount of furan no-bake binder used is usually 0.7-0.9 %, based on sand weight. Catalyst levels generally are from 20-40% based on the weight of the binder [5]. The acid catalyzed FNB does not work well with high acid demand value silica-type sands, and very basic (alkaline) aggregates, such as olivine. [1] Figure 1 indicates generally available organic binder classification.

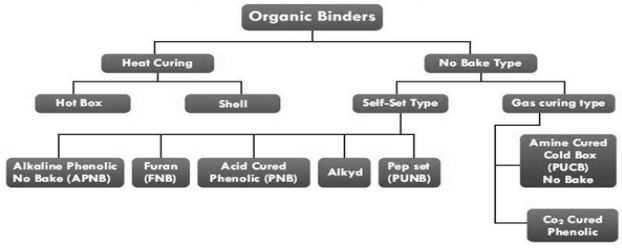

Fig. 1. Organic Binder Classification

2. Work Methodology

2.1. Experimental details

Furan resin is getting popularity in foundry industry now a day because of its self setting capacity of binder at room temperature. For our study Furan Binded sand sample was prepared using industrially available resin and catalyst. For preparation of Furan binded sand samples ordinary river washed sand, Resin and Catalyst of () were used. Weight ratio of Sand, Resin and Catalyst was used 100:0.85:0.30. It was necessary to identify the starting constituents before calculating gas amount releasing because of the thermal decomposition of the furan. To identify the Resin and Catalyst Gas Chromatography-Mass Spectrometry (GC-MS) study was carried out at NFDD center of Saurashtra University using JEOL GCMATE II GC-MS. GC-MS data was obtained up to 200 ^{o}C. Based on the data collected in the GC-MS characterization chemicals formula of the Resin and Catalyst were confirmed. To identify bonds present in the furan binded sand Fourier Transform Infrared Spectrum was obtained in the NFDD center of Saurashtra University using NICOLET 100I instrument at an ordinary tenperature. Presences of the different bonds were confirmed from the obtained FTIR spectrum. To observe weight loss from the furan binded sand in the different regions of the temperature Thermo gravimetric Analysis (TGA) was carried out using Netzsch DSC with heating rate of 10 ^{o}C / min. From the obtained data various weight loss regions were identified. To identify and quantify gases releasing from furan binder sample of gas was collected using medical syringe from sand mold. Collected sample of gas was analyzed using GC-MS characterization using JEOL GCMATE II GC-MS. Based on the results obtained from the GC-MS analysis amount of gases were calculated and compared with standard gas exposure limits.

3. Result and Discussion

To identify the starting materials used for the preparation of furan resin, GC-MS analysis was done. Obtained GC-MS spectrum and the matched library of Resin are shown in figure 2. In obtained spectrum molar weight is calculated around 98 g/mole. Spectrum is best matching with the Furfuryl alcohol with retIndex 885 which confirms that the resin which we are using for the binding process is Furfuryl alcohol. The chemical formula of the resin is $C_5H_6O_2$ and chemical name of the resin is furan-2-ylmethanol. Molar weight of the given rein is 98 g/mole.

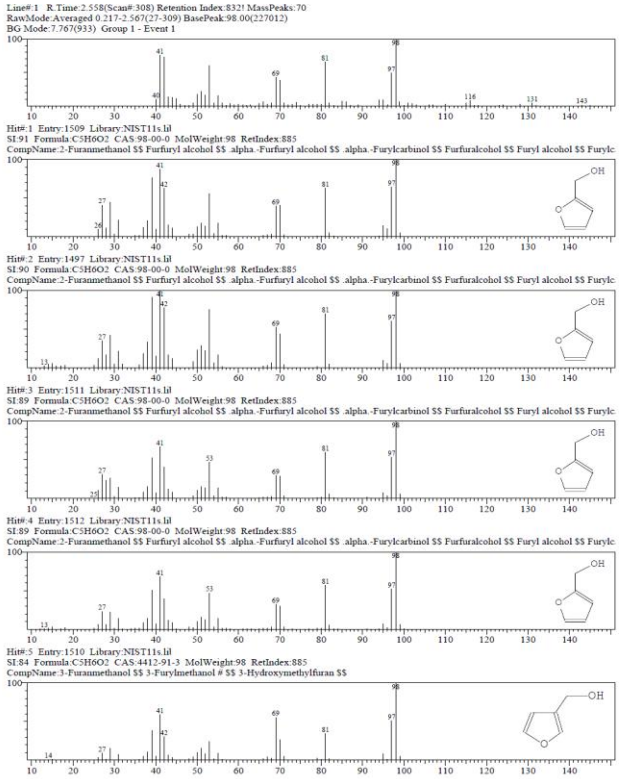

Fig. 2. GC-MS spectrum of Resin and matching library

Figure 3 shows GC-MS spectrum and matched library of catalyst used in the process. Obtained spectra is perfectly matching with the GC-MS spectrum of P-Toluenesulfonic acid with RetIndex 1454. Molar weight of the characterized chemical is 172 g/mole. So, it is confirmed that the catalyst which we are using for curing is P-Toluenesulfonic acid. Chemical formula of the obtained material is $C_7H_8O_3S$. Now it is confirmed that the chemicals which we are using for making furan binded sand are alfa-Furfuryl alcohol and Benzenesulfonic.

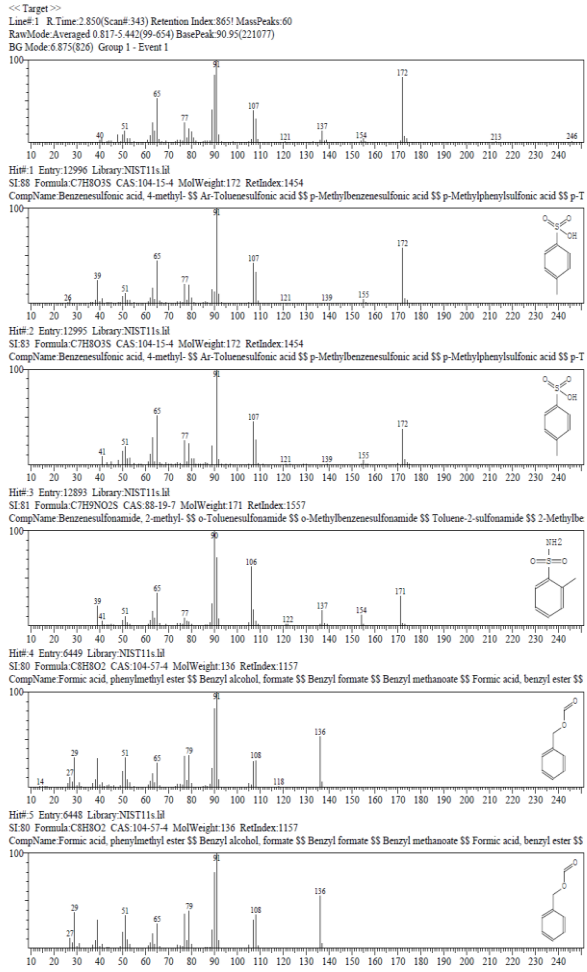

Fig. 3. GC-MS spectrum of Catalyst and matching library

For preparation of 1 kg furan binded sand 0.85% of Resin and 0.3% of catalyst are used. In the curing process of furan binder 2.55 g of P-Toluenesulfonic acid is added in 8.5 g of Furfuryl alcohol. As shown in figure during curing process polymeric chain of furan would be formed. In the presence of sulfonic acid polymer chain of Furan would be form and a small amount of water releases. For binding of 1 kg of sand, amount of resin and catalyst used for the process and amount of product and catalyst can be seen in table 1.

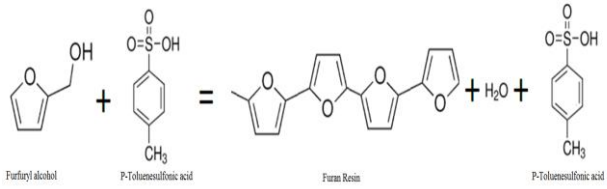

Fig. 4. Chemical reaction showing polymerization process of the Furan resin

Table 1.
Amount of starting ingredients and the product releasing in the polymerization process

Starting Ingredients	Amount (g)	Product Name	Amount (g)
Furfuryl alcohol	8.5	Furan Resin	6.939
P-Toluenesulfonic acid	2.975	P-Toluenesulfonic acid	2.975
		Water	1.56

As shown in Table 1 certain amount of Furan Resin, P-Toluenesulfonic acid and water can be observed with sand. In the paralysis process of the furan binded sand these compounds would decompose and because of the decomposition of these compounds emission of the gases can be observed.

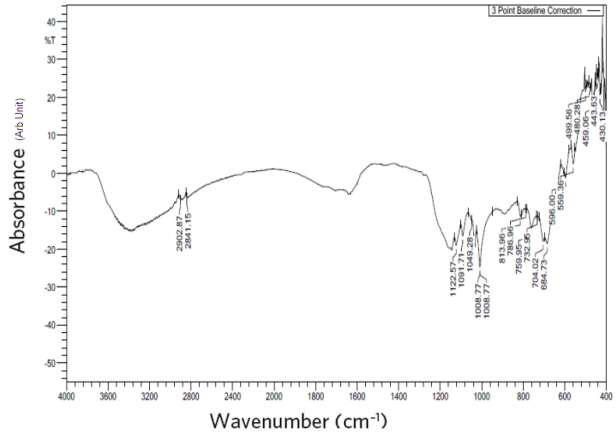

Fig. 5. FTIR spectrum of Furan Binded Sand

FTIR spectrum of furan binded sand can be observed in figure 5. In the obtained spectrum various abortion wavelengths can be observed. These absorbing picks show presence of the various bonds in the Furan Binded sand. Presence of the peak at 2902 and 2901 cm^{-1} wavelength is due to the presence of the CH_2 asymmetric stretch bonds which confirms the presence of the Sat. Hydrocarbon group [6]. Presence of the peaks at 1122, 1091 and 1049 cm^{-1} can be seen because of the presence of the weak C-H bond present in the Furan Ring [7]. Peak observed at 1008 cm^{-1} is due to the presence of C-O-C stretching in the Furan ring. Bond of C-H out of plan deformation is confirmed with the presence of the peak at 813 and 786 cm^{-1}. The presence of the deformation vibration (C=C) can be conformed due to the presence of the between 759-684 cm^{-1}. Absorption at 596 and 559 cm^{-1} is due to the presence of S-O bending in upper part of sulfonic acid. Absorption of the spectrum bellow 500 cm^{-1} is due to the presence of the metal oxide bonds.

3.1. TG Analysis

Figure 6 shows different weight loss regions of regions of the Furan binded sand. Almost 2 % loss of weight can be observed in the temperature range 50 to 150 ^{o}C due to the loss of water releasing during the curing process. Los of weight during in 150 to 700 ^{o}C is mainly due to emission of different gases because of the decomposition of the furan ring. Main gases emitting from Benzene sulfonic acid catalyzed furan binded sand are Furan, Toluene, Ethynylbenzene, Styrene, 1,2-Benzenedicarboxylic acid, Hexadecanoic acid and Thiophene.

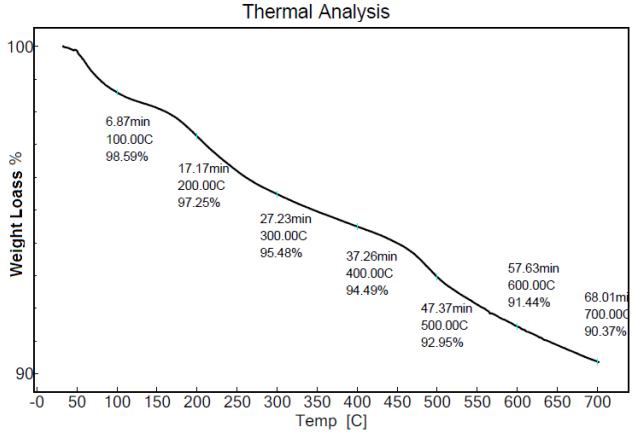

Fig. 6. TGA of Furan Binded Sand

In the present work we used 100:0.85:0.30 ratios of Sand, Resin and Catalyst. So for the preparation of 1Kg furan binded sand 8.5 g of resin was used and 2.95 g of catalyst was used for curing process of resin. In the curing process of furan 1.56 g water releases and we could obtained 6.93 g of furan binder. Total amount of resin and catalyst remains in this sample is 9.88 g which decomposed in above mentioned gases at high temperature. For making 1 kg of furan binded sand, total amount of Furan and Catalyst is 9.88 g. Figure 6 shows mean temperature variation with respect to distance from molten metal and with respect to time in furan binded sand. As shown in figure temperature is very high closer to the molten metal and rate of increment of temperature is high in the region closer to the molten metal. While in other part of the mold temperature reduces as we go far from the molten metal. These causes decomposition of furan resin in different gases in different amount as listed in Table 2.

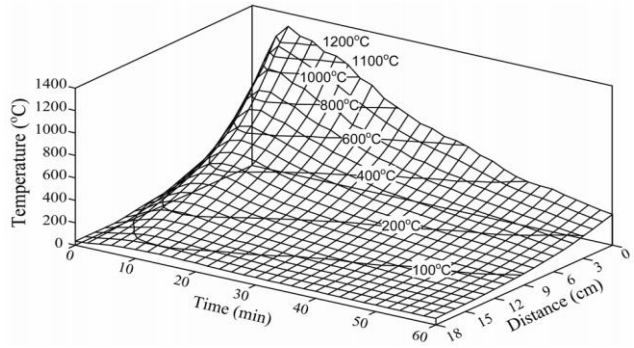

Fig. 7. The plot of the mean temperature versus distance and time of furan sand mold in founding process. The distance is the position from the interface of molten iron and mold to outside edge of the mold [8]

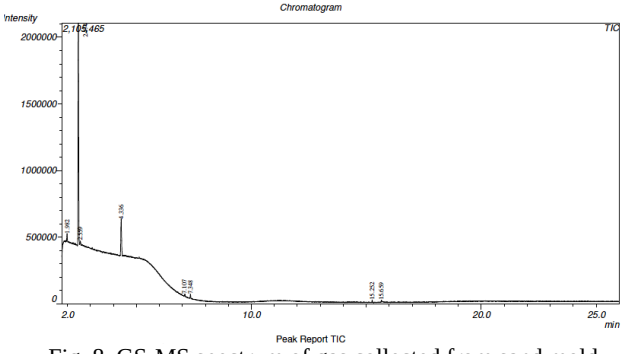

Fig. 8. GS-MS spectrum of gas collected from sand mold

Figure 8 represents GC-MS spectrum of gas Sample collected from sand mold. Various picks can be observed in the obtained data. These data was analyzed by matching it with the available library. 2-Methylfuran-Benzene, Toluene,Ethynylbenzene, Styrene, 1,2-Benzenedicarboxylic acid, Hexadecanoic acid and Thiophene are assigned to the peak respectively. Obtained results from GC-MS and their results are listed in Table 2. Table 2 shows area of analyzed peak, % Area covered by each peak in graph, Name of gas assigned with the peak their Molar weight, % of Weight, weight in gas and directive permissible limit.

Table 2.
Amount of gas indentified with GC-MS characterization

Peak No.	R. Time (Min.)	Area	Area (%)	Name of Gas
1	1.98	105805	2.68	2-Methylfuran
2	2.47	2955542	74.83	Benzene
3	2.56	63515	1.61	Thiophene
4	4.34	663396	16.80	Tolune
5	7.11	38890	0.98	Ethynylbenzene
6	7.35	67717	1.71	Styrene
7	15.25	19791	0.50	1,2-Benzenedicarboxylic acid
8	15.66	35135	0.89	Hexadecanoic acid

Peak No.	MW (g/mole)	% of Weight (%)	Weight in Gas (μg/m^3)	Directive Permissible Limit [10-11]
1	82.10	2.20	0.09	1
2	78.11	58.45	2.54	5
3	84.14	1.35	0.05	1
4	92.14	15.48	0.57	20
5	102.13	1.00	0.03	3600
6	104.15	1.78	0.06	100
7	166.14	0.83	0.02	5
8	256.43	2.28	0.03	5

Weight in gas was calculated using ideal gas law

$$PV = nRT \tag{1}$$

Where,
P is the pressure
V is the volume
n is the amount (in moles)
R is the ideal gas constant having value 0.08206 L bar mol^{-1} K^{-1}
T is the temperature of the gas

In the above equitation amount of gas in mole is,

$$n = \frac{m}{MW} \tag{2}$$

Where, m is weight of gas and MW is Molar Weight of gas.
So,

$$m = MW \cdot \left(\frac{PV}{RT}\right) \tag{3}$$

Equ.3 was used to obtain weight of the gas present in the samples obtained from the gas collected from sand mold. Ito calculate the weight of gases Pressure was considered 1 bar. volume is considered 1 ml, R is 0.08206 L bar mole^{-1} K^{-1} and Temperature T is 300 K. After identification of gases in the sample average molar weight of the gas was calculated using equation,

$$average\ molecular\ weight\ MW = \sum X_i \cdot M_i \tag{4}$$

Where,
X_i is mole percentage of gas in sample and
M_i is Molar weight of gas.

Using equ. 4 the value of molar weight was obtained 83.38 g/mol. Substituting the value of average molar weight (MW) in equ.3 weight of the gas m was calculated and the obtained value of m is 0.003389 g/L. Weight of each gases were calculated considering the total weight of gas 0.003389 g/L and multiplying it with the weight fraction obtain in the GC-MS data. . In the given table gas emission standards are mentioned which shows permissible value of these gases in foundry [9] [10]. As we can see in the table, all calculated values of gas emission per second are below permissible limit. Obtained result in Table 3 clearly shows that gas emission from furan binded sand is bellow permissible limit.

4. Conclusions

As we can conclude from the obtained data resin and catalyst are Furfural alcohol and Toluene Sulfonic acid. H-C bonds are observed in furan binded sand which helps to hold the sand particles with each other. This property of furan resin shows the binding nature. From TG analysis emission of various gases is confirmed and their amount is obtained. Total amount of the gases releasing during a day was calculated based on the calculation and it was compared with the international standers of permissible gas emission limits in a foundry. It was confirmed that the gas emitting in the pyrolysis process are below permissible standards. From the results it can be concluded that emission of HAPs considerably decreases in pyrolysis of Benzene sulfonic acid catalyzed Furan resin.

Acknowledgements

Authors are really acknowledging the help and support from Central Salt and Marine Research Institute (CSMCRI), Bhavnagar, National Facility for Drug Discovery (NFDD), Rajkot and Krislur Castomech Pvt. Ltd., Bhavnagar.

References

[1] Ireland, E., Chang, K., & Kroker, J. (2002). New horizon in nobake binder technology. *AFS Transactions.* 02-025, 1-7.

[2] Ambidge, P., & Biggins, P. (1985). Environmental problems arising from the use of chemicals in moulding materials. *BCIRA Journal*. BCIRA Report, July 296-308.

[3] Twong, D.L. (1992). *Waste management study of Foundries major waste streams: phase 1*. WMRC is a division of the Illinois Department of Natural Resources, TR-E11 Nov.

[4] Kanicki, D. (1994). Metal casting's versatility offer [sic] users a competitive edge. *Designers & Buyers, Guide to Selecting Casting Processes I. Casting World/Modern Casting Publication*. 5-10.

[5] Acharya, S.G., Vadher, J.A., Sheladiya, M.M. (2015). Identifying path to defect free iron casting through evaluation of sand of FNB mould system. 3RD Afro - Asian International Conference on Science, Engineering & Technology, AAICSET – 2015, 2-3 May (72-76). ISBN: 9-780993-909238

[6] Renhe, H., Hongmei, G., Yaoji, T. & Qingyun, L. (2011). Curing mechanism of furan resin modified with different agents and their thermal strength. *China Foundry.* 8(2), 161-165.

[7] Zhang, H., Zhao, H., Zheng, K., Li, X., Liu, G. & Wang, Y. (2014). Diminishing hazardous air pollutant emissions from pyrolysis of furan no-bake binders using methanesulfonic acid as the binder catalyst. *J Therm Anal Calorim.* 116, 373-381.

[8] Liang, J.J. & Tsay, G.S. (2010). Composition and yield of the pernicious and stench gases in furan resin sand model founding process. *J. Environ. Eng. Manage*. 20(2), 115-125.

[9] Rangarajan, R. (2009). *Air Quality Monitoring Regime in India.* An Overview Pollution Monitoring Series: Briefing Note 1.

[10] Wong, C.M., Crawford, R.W. & Yost, R.A. (1985). An Evaluation of Triple Quadrupole Ms/Ms For On-Line Gas Analyses of Trace Sulfur Compounds From Oil Shale Processing. *UCRL- 87189, REV. 1*