Asian Journal of Science and Applied Technology
ISSN: 2249-0698 (P) Vol.7 No.1, 2018, pp.11-16

DOI: https://doi.org/10.51983/ajsat-2018.7.1.1025

Analysis of Chemically Bonded Sand Used for Molding in Foundry

Digvijay A. Mhamane[1], Suyog B. Rayjadhav[2] and Vasudev D. Shinde[3]
[1&2]Junior Research Fellow, [3]Professor
[1&2]SMART Foundry 2020-DKTE, [3]DKTE, Kolhapur, Maharashtra, India
E-Mail: digvijaymhamane@gmail.com

(Received 11 January 2018; Revised 28 January 2018; Accepted 19 February 2018; Available online 26 February 2018)

***Abstract* - In casting industry the selection of mold material and molding method is challenging task. There are several types of molding methods, but over 70% of all metal castings are generally developed by means of sand molding (sand casting). Sand casting has two processes such as, green sand casting and chemically bonded sand casting process. This paper focuses on chemically bonded sand casting i.e. no-bake sand system (self-hardening system), among from all types of no-bake sand system, alkaline phenolic ester cured (ALPHASET) and furan acid cured no-bake system are preferably discussed. Curing mechanism of all type of no-bake systems are shown along with detailing about ALPHASET and furan no-bake sand system.**

***Keywords:* Alkaline phenolic resin, Furan, Resole Resin No-bake sand system, Curing Mechanism**

I. INTRODUCTION

The foundry industry is one of the versatile sectors of industries. The several ways are used in foundry industry to develop metal parts. It includes such processes as centrifugal casting, permanent mold casting, evaporative pattern casting, and sand casting. The main process divisions for manufacturing castings include molding and casting. Molds and cores are the consumable parts of sand casting. For hollow castings Cores are needed and after solidification of metal, cores must be removed [4]. The figure 1 shows classification of sand molds by molding technology.

According to mold materials there are three types of mold i.e. metal dies, sand molds and ceramic mold. Over 70% of all metal castings are generally developed by means of sand casting. Majority sand molds and cores are made of silica sand, because it is the most easily available molding component. It has lower cost of tooling, broad scope of metals and fewer limitations in part geometry, especially when compared to permanent mold processes [2] [10].

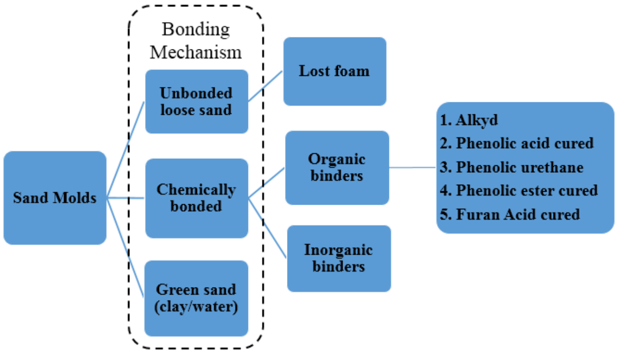

Fig. 1 The Classification of Sand Molds by Molding Technology

II. SAND MOLDS

Among from all types of sands 'silica sand' is basically used for sand molding and the desired properties of silica sand is represented in Table I. The refractoriness of sand is directly proportional to amount of SiO2 (%) but it is inversely proportional to amount of iron oxide. The loss of ignition depends on organic impurities. The percentage of CaO causes increase in acid demand value. Another reason of refractoriness reduction is higher content of K2O and Na2O. Also high acid demand value adversely effects on binders with acid catalyst [3].

TABLE I PROPERTIES OF SILICA SAND FOR FOUNDRY USE

Particulars	Allowable Content
SiO_2	95–96% min
Loss on ignition	0.5% max
Fe_2O_3	0.3% max
CaO	0.2% max
K_2O, Na_2O	0.5% max
Acid demand value to pH4	6 ml max

The acid demand value (ADV) depends on the chemical composition of the sand. A catalyst requirement of cold-setting, acid catalyzed binders is selected as per ADV. If sands has ADV about 6-10 ml, it requires large quantity of acid catalyst and sand with ADV greater than10–15 ml are not acceptable for acid catalysed binder systems. Zircon has low ADV and it can be used with all chemical binder systems. Chromite has somewhat higher ADV than other sands which requires high acid catalyst with furan resin. Olivine has a very high acid demand and is not suitable for use with acid-catalyzed binders.

To generate the bonds among the sand particles different bonding mechanism are used such as green sand (clay and water), un-bonded loose sand with lost foam and chemically bonded sand. Binders are adopted to reinforce the molds and cores, which gives better casting quality. While the application of binders in development of mold is increasing, most sand castings involves green sand molds, which are made of sand, additives, and clay as well as chemically bonded sand molds as per the application [1].

III. ORGANIC AND INORGANIC CHEMICAL BONDED SAND

Nowadays, chemical bonded sand is widely used for molds and cores. The ways of binder's application as:

A. Triggered Hardening

Sand and binder are mixed and blown or rammed into a core box. Little or no hardening reaction occurs until triggered by applying heat or a catalyst gas. Hardening then takes place in seconds. The process is used for mass production of cores.

B. Self-hardening Mixtures

It is the combination of sand, binder and hardening chemical. The binder and hardener start to react immediately with each other and mold or cores are to be formed accordingly. Further hardening is in process until strong enough to allow casting. The sand required for molding has average grain size 250–300 microns (AFS 45–60), which has low acid demand value, less than 6 ml for acid-catalyzed systems. Rounded shape of sand grains gives low binder additions and flow ability. If sand has low fines then it requires low binder additions.

The method is usually used for large molds and for series production [3].The binders are mostly based either on organic resins or inorganic binders, the Table II represents organic as well as inorganic binders and their chemical formulae. Inorganic binders such as cement, which was the earliest of the chemical binders to be used, ethyl silicate, which is used in the Shaw process (The Shaw process is a precision casting process capable of the production of accurate moulds with excellent surface finish and metallurgical integrity) and for investment casting, and silica sol, which is used for investment casting [3].Sodium silicate (inorganic binder) has low cost, low toxicity, cleanliness but it has limited storage, low strength, and low collapsibility of the mold.

TABLE II ORGANIC, INORGANIC BINDERS AND THEIR CHEMICAL FORMULAE [13]

Inorganic substance		**Organic substance**	
Binder	**Chemical formulae**	**Binder**	**Chemical formulae**
Bittern	$MgCl_2$	Phenolic resin	$(C_6H_5OHCH_{20})n$
Sodium phosphate	Na_3PO_4	Furan resin	$(C_5H_4OCH_2O)n$
Alumina cement	$(CaO)(Al_2O_3)$	Pitch	$C_{10}H_{10}$ etc.

In organic binders, because of the low values of fixed carbon ratio, urea–formaldehyde and epoxy resins are considering as a primary binder and they are thermosetting resins. However, phenolic resin, furan resin, and pitch have high fixed carbon ratio, so that they are considered as main binders. Phenolic resin includes both novolak and resoles resins. Also the Table III shows that ratio of fixed carbon of organic compound.

TABLE III RATIO OF FIXED CARBON OF ORGANIC COMPOUND [13]

Type	**Ratio of fixed carbon (%)**	**Type**	**Ratio of fixed carbon (%)**
Coal tar pitch	52.5	Melamine resin	10.2
Phenolic resin	52.1	Epoxy resin	10.1
Furan resin	49.1	Urea–formaldehyde resin	8.2
Poly-acrylonitrile	44.3	Natural rubber	0.6
Butadiene rubber	12.1	Polyester resin	0.3
Cellulose acetate	11.7		

IV. ORGANIC NO-BAKE SAND SYSTEM (SELF-HARDENING)

The no-bake sand system or self-hardening sand system is basically works at the room temperature; it is curing of two or more binder components after they are mixed with sand. Curing of this mixture begins immediately after all parts of system are combined with each other [1] [4].

TABLE IV SAND PREPARATION SYSTEM

S. No.	**Content**	**Resin (By weight of sand)**	**Hardener (By weight of resin)**	**Catalyst (By weight of resin)**
1	Alkyd No-bake System	1-2%. (Alkyd oil type resin)	18 to 20% (Isocyanate)	2 to 10% of resin by Wt. (Amine)
2	Phenolic urethane No-bake System	0.7 to 2% (Phenol formaldehyde)	40-45% (Polymeric MDI-type isocyanate)	0.4 to 8% of resin by Wt. (Amine)
3	Phenolic Acid Cured No-bake System	1-2% (Phenol resin)	40-45% (Aldehyde-Acidic Agent)	-
4	Alkaline phenolic ester cured No-bake system	1.5 - 2% (Alkaline phenolic resole)	About 20 % (Aliphatic ester)	-
5	Furan Acid cured No-bake System	0.9-2.0% (Furfuryl alcohol)	20-50% (Sulphonic Acid)	-

A. Alkyd No-bake System

This system has three-components such as; considered as Part A and Part B is liquid amine/metallic catalyst and polymeric methyl di-isocyanate (MDI) is Part C. an alkyd oil type resin (Part A) is generally added with sand in between 1 and 2% of sand weight. The liquid amine as part B (catalyst), is used 2 to 10% by weight of Part A, which is mixed as a separately or along with Part A. 18 to 20% of the Part C isocyanate is added by weight of (Part A) an alkyd oil type resin. Due two separate curing stages, the curing mechanisms of Alkyd No-bake System are difficult to understand. The two stage curing mechanism is shown below,

Alkyd + NCO (polymeric isocyanate) (partial cross-link) + Urethane catalyst →Alkyd urethane
Alkyd + O2 + Metallic driers →Rigid cross-linked urethane

This system may be converted to two-part system by pre-combining Parts A and B when the Part B catalyst added to the resin, which controls the work/strip time.

B. Phenolic Acid Cured No-bake System

This is two-part no-bake system, phenol resin is treated as first part and aldehyde is the second part. By weight of sand, 1-2% of phenolic resin is added during molding as part I, the acidic agent i.e. aldehyde is added in between 40-45% of weight of phenolic resin. The curing agent required for this system is a strong sulfonic acid type, however, phosphoric acids is not able to permit fast curing of phenolic resins at the rate required for foundry applications.

The curing mechanism of phenolic acid cured no-bake system is:

Phenolic resin + Acid catalyst →Cured polymer + Water

The curing agent actuates condensation reaction of the resin and boosts the cross-linking reaction. The condensation reaction develops water molecules, which will dilute the acid catalyst that slows the rate of cure.

C. Phenolic Urethane No-bake System

This system is made of three-part, such as phenol formaldehyde resin considered as Part I; Part II is a polymeric MDI-type isocyanate; and, an amine catalyst is treated as Part III. The curing mechanism of Phenolic urethane no-bake system is:

Liq. phenolic resin (I) + Liq. polyisocyanate (II) + Liq. amine catalyst (III) →Solid resin + heat

The binder level required for this system is 0.7 to 2% by the weight of sand. Part II is in terms of 40-45% on the basis of part I. The third-part catalyst level is also by the weight of Part I, and it is 0.4 to 8%. This system does not have the problems regarding curing or deep-set, because air does not necessary for setting and no other by-products generation at the chemical reaction between Part I and Part II, it forms a urethane bond only.

D. Alkaline Phenolic Ester Cured No-bake system

This system is also called as ALPHASET System, which is new and unique technology developed and patented by Borden Chemical. The alkaline phenolic ester-cured no-bake system is a two-part system, which has a (water-soluble) alkaline phenolic resin and (liquid) ester co-reactants. During sand preparation, 1.5 - 2 % of the alkaline resole by weight of sand is first blended into the sand, followed by about 20 % of an aliphatic ester which is based on resin weight. The curing mechanism for ALPHASET is started by the liquid ester reacting with alkali in the phenol resin, to form the alkali metal salt of the acid component of the ester (1st stage) [12].

Alkaline phenolic resin (RESOLE) + ester co-reactant + alcohol →polymerized phenolic resin + alkaline salts

A secondary reaction is thought to occur when the partially polymerized resin contacts heat during the pouring of liquid metal operation, yielding an extremely rigid structure (2nd stage) [12]. The co-reactants are organic esters and their blends, typically triacetin and butyrolactone. In terms of speed, dibasic esters cure the slowest, followed by triacetin, with butyrolactone the fastest. Phenolic alkaline resin is not very sensitive to sand ADV. The fact that it is a makes the system is less sensitive to moisture because of water-soluble aqueous nature of resin, and it can allow up to 0.3% water in the sand. Resole resin is the product of phenol. The phenol is forms by cumene as shown below, figure 2 shows formation of phenol from cumene [13][1].

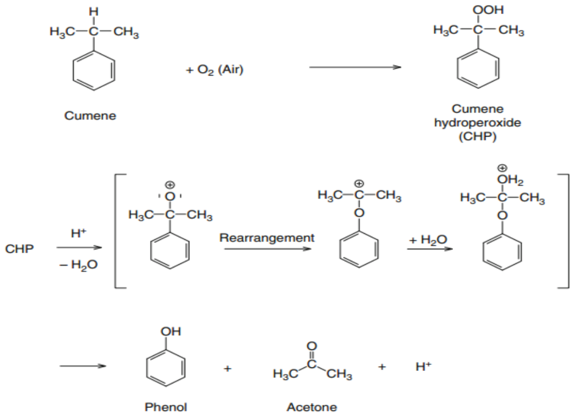

Fig. 2 The Phenol formation from Cumene

Resole resin is basically formed by several ways such as,

1. Resole Resin Formation from phenol; Figure 3 shows that chemical reaction between Phenol and formaldehyde at 70-1000C [7]

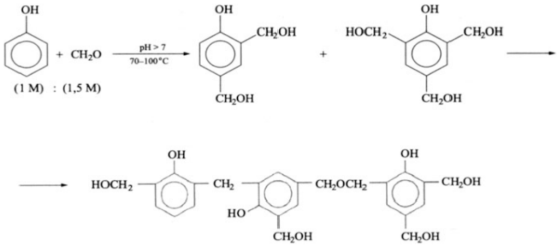

Fig. 3 The Resole resin formation from Phenol

2. Resole and Novolak resin formation from chemical reaction between Phenol and formaldehyde by molar ratio as Acidic and Basic [13] as shown in figure 4.

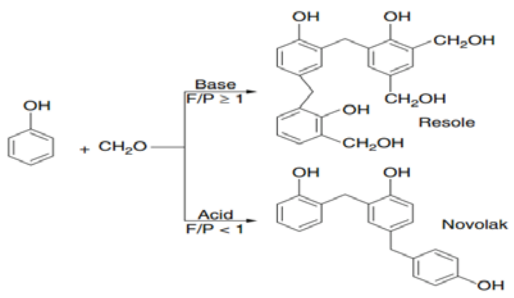

Fig. 4 The Resole resin Formation by Molar Ratio

3. Resole Resin formation by condensation between Phenol and formaldehyde at temperature 60-1000C as shown in figure 5 [13]
4. Temperature range above 600C, condensation reactions of methylol phenols with phenol and/or methylol phenols occur and lead to pre-polymer or the desired resole resin.
5. Resole resin formation by reaction between Phenol and methylene glycol.

A basic alkaline catalyst and (molar) excess formaldehyde is used to make resole resins. First, phenol reacts with methylene glycol to form methylol phenol as shown in figure 6.

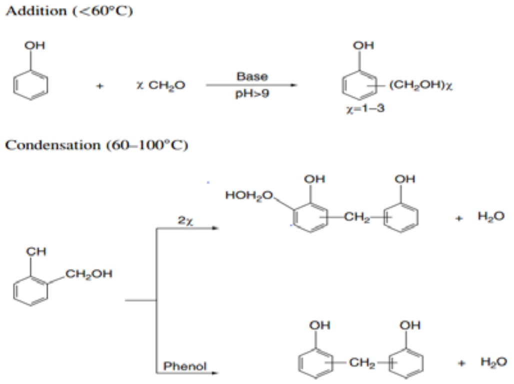

Fig. 5 The Resole resin formation by Condensation

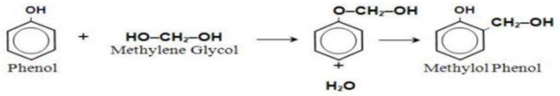

Fig. 6 Methylol phenol formation

Formation of longer chain methylol phenolic due to reaction of Methylol phenol with itself as shown in Fig.7.

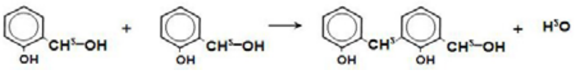

Fig. 7 Longer chain of Methylol

Or formation of di-benzyl ether as shown in figure 8.

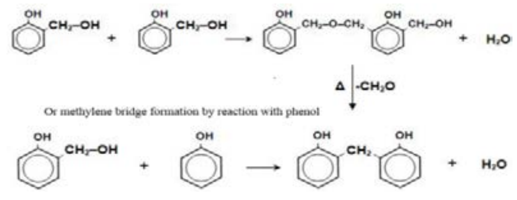

Fig. 8 The formation of di-benzyl ether and Resole resin

The phenolic resoles possess the following properties such as, low levels of free phenol and formaldehyde, also low water levels and desirable viscosity range. It has fast curing rates in addition with acid and good plasticity followed by curing. Due to these properties, this resin gives uniform sand coating, ease of compaction, low odour. Long period of stripping during which the molds or cores can be "stripped" (i.e., removed or de-molded from the pattern or core box), coupled with desirable curing times. It has 90-95% of reclamation feasibility. The rich carbon supply and very low nitrogen level of the residual phenolic resin binders afford castings of high surface quality. The phenolic resole has higher hot strength and more elastic nature when cured (as compared to furan)

E. Furan Acid Cured No-bake System

This is two parts no-bake system. The basic raw material for this system is "furfuryl alcohol" and acidic curing agent. This binder can also be modified with urea, phenol, formaldehyde, and other additives, which are of non-reactive or reactive type of additives. The binder (i.e. furfuryl alcohol, which is a colorless to pale yellow liquid) as part A is used 0.9-2.0% based on weight of sand. Acid catalyst as part B (hardener) is used in between 20-50% based on the binder weight.

The two main types of catalysts are the phosphoric acid-based (70-85% Phosphoric acid) and the sulfonic acid-based (solutions of benzene-sulfonic acid (BSA) or Toluene-sulfonic acid (TSA), or other sulfonic acids. The time required for curing reaction depends on the catalyst type and/or percentage of catalyst, at constant temperature and for same type of sand. The curing mechanism of furan no-bake is shown in figure 9.

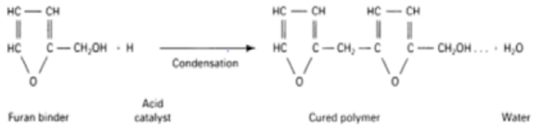

Fig. 9 The Curing Mechanism of Furan Acid Cured No-Bake System

Furan no-bake casting process uses resins and acid catalyst to form a binder system. Since, the resins are acid catalyzed, sands should have a low ADV, less than 6 ml. However this process produces castings with high strength and good surface finish. Hence this method is suitable for producing accurate dimensioned castings. The furan resins possess the following properties, the viscosity lower than that of phenolic resin. It is considered to be less temperature dependent, especially when lower ambient temperatures retard curing. Due to the brittle nature of the cross-linked furfuryl alcohol polymer, it easier to remove from the sand grains by attrition methods. Testing of reclaimed sand is needed for LOI, ADV, grain size and temperature. Sand (reclaimed) with high LOI causes to excess fumes during casting [13] [3]. Among from all no-bake systems every system has its own characteristics, and then also they can be distinguished with respect to different parameters such as, stripping time, bench life, high temperature properties, gas evolution etc. as shown in Table V.

TABLE V A COMPARISON OF PROPERTIES OF NO-BAKE BINDER SYSTEMS

Parameter	**Process**				
	Acid catalysed		**Ester cured Alkaline phenolic**	**Alkyd**	**Phenolic urethane**
	Furan	**Phenolic**			
Stripping time (min.)	20-25	30-35	14-16	60	5-8
Bench Life (min.)	7-8	5-10	4-12	10-12	2-3
Fumes evolution at pouring	Mild pungent fumes	Pungent fumes	No Fumes	Pungent Fumes and eye irritation	Pungent Fumes and eye irritation
Veining properties	Very Low	Very Low	No Veining	Very Low	Very Low
Relative tensile strength	High	Medium	Medium	High	Medium
Scans and Inclusions	Least Tendency	Least Tendency	Least Tendency	High Tendency	High Tendency
High temperature properties	Very Good	Good	Excellent	Medium/ Low	Medium
Ease of shakeout	Good	Fair	Good	Poor	Good
Humidity resistance	Fair	Fair	Excellent	Good	Good
Optimum (sand) temperature, °C	27	27	27	32	27
Flow-ability	Good	Fair	Good	Fair	Good

V. CARBONIZATION MECHANISM

Carbonization is nothing but the conversion of an organic substance into a carbon containing residue through destructive distillation or pyrolysis. Carbonization mechanism for phenolic hydroxyl group, which is basic element of “Phenolic Acid, Phenolic Urethane, Alphaset” no-bake system etc. are as follows; which is used in; Carbonization of phenolic resin is happens at the temperature above 3000C as discussed below,

At about 3000C = dehydration reaction of the phenolic hydroxyl group and release of oxygen.

At about 4000C = Carbonization progresses and Reduces both a weight and strength during pyrolysis.

At 5000C and above = the resin carbonizes almost completely.The carbonization of phenolic hydroxyl group is as shown in figure 8,

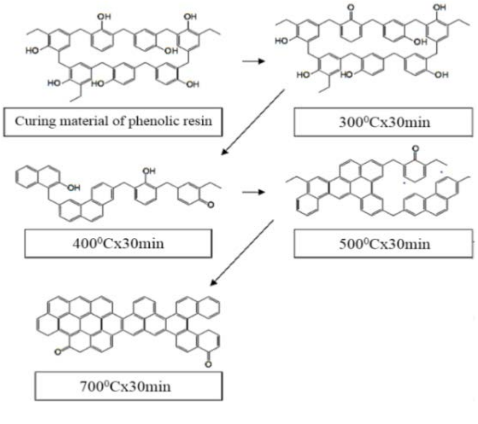

Fig. 8 The Carbonization Mechanism of Phenolic Hydroxyl group

Similarly, carbonization of all organic resins are happens, and at higher temperature (>8000C) thermal reclamation of organic resin bonded sand can be achieved. At higher temperature some pollutants are evolved, which are environmentally harmful. The evolved harmful pollutants are shown in Table VI.

The BTEXs (Benzene, Toluene, Ethyl-benzene, Xylenes) and polycyclic aromatic hydrocarbons (PAHs) are few types of pollutants. Three samples of sand are considered with different no-bake system as, 100% fresh silica sand, 50% of fresh and reclaimed sand each, and 100% reclaimed sand. The different values of Table VI shows that alphaset no-bake sand system has less environmental impact than furan no-bake sand system.

VI. DISCUSSION

In casting industry the selection of mold material and molding method is challenging task. No-bake sand system (self-hardening system) is the better option for development of quality casting with minimum efforts. The binders used in this system are of either organic or inorganic type, but organic binders are having better environmental aspects.

Among from all organic binders, alkaline phenolic binders and furan binders (organic binders) are widely used for better casting quality. Resole polymer is used as resin and triacetin or butyrolactone as a co-reactant (ester cured) in alkaline phenolic, while furfuryl alcohol polymer as resin and sulphonic acid as hardener in furan no-bake sand system.

According to Table VII Alphaset system has higher environmental acceptability. As casting quality point of view, both furan and alkaline phenolic no-bake system has better desirability. The emission from the “Alphaset” system is 2 to 5 times smaller than the furan no-bake system (even of the furfuryl alcohol content < 25%) [7].

TABLE VI THE POLLUTANTS GENERATED DURING CARBONIZATION

Pollutants (mg/Kg)	**Furan acid cured**			**Alkaline Phenolic Ester cured (ALPHASET)**		
	100% Fresh sand	**50% Fresh 50% Reclaimed**	**100% Reclaimed**	**100% Fresh sand**	**50% Fresh 50% Reclaimed**	**100% Reclaimed**
Benzene	654.5	1198.6	1770.4	246.7	332.2	446.3
Toluene	10.1	89.0	122.1	2.1	5.3	8.4
Ethyl-benzene	0.6	1.8	2.2	0.3	0.3	0.6
Xylenes	1.2	7.7	11.8	0.02	0.02	0.5
PAHs	11.76	23.64	25.56	5.28	6.87	5.69
LOI %	1.32	2.18	3.15	0.91	1.27	1.40
Volume of gases (dm^3/Kg)	14.95	19.33	24.67	11.03	13.77	16.77

TABLE VII EFFICIENCY OF BINDER SYSTEM [MODIFIED FROM10]

S. No.	**Parameters**	**Furan No-bake system**	**Phenolic Urethane No-bake system**	**Ester Cured Phenolic No-bake system (Alphaset)**
1	Productivity	Moderate	Highly desirable	Less desirable
2	Casting Quality	Highly desirable	Moderate	Highly desirable
3	Environmental acceptability	Moderate	Less desirable	Highly desirable

VII. CONCLUSION

Among from all no-bake systems, every system has its own characteristics. Alkaline phenolic and alkyd no-bake system has higher bench life. Stripping time of acid cured phenolic no-bake system is more. Phenol and resole are the basic elements of curing mechanism of Alphaset. According to curing time, compressive strength of mold is goes on increasing up to certain limit of time. High temperature pouring of molten metal in mold cavities causes initialization of decomposition of organic binders. The decomposition of organic binders initiates above 3000C. By holding this resin bonded sand for 30 minutes above 5000C temperature, complete decomposition of organic bonders will happen. Some harmful gases evolve from resin bonded sand during heating at higher temperature. The values of BTEX i.e. benzene, toluene, ethyl-benzene, xylenes and PAHs i.e. polycyclic aromatic hydrocarbons group) from phenolic ester cured no-bake system are smaller than other no-bake sand system. Alkaline phenolic ester cured no-bake sand system has better casting quality and lower environmental impact. So, it is concluded that, alkaline phenolic ester cured no-bake sand system is preferable for foundry industry.

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