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Evaluate Sulphur Diffusion at Mould-Metal Interface in No-Bake Mould System

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Abstract

Casting process takes a major percentage of manufacturing products into consideration. No-bake casting is swiftly developing technology for foundry industries. In the no-bake family, furan no-bake casting process employs resins and acid catalyst to form a furan binder system. However, this process configures castings with augmented strength and quality surface finish. Compressive strength, transverse strength and tensile strength of moulds are also high in this furan binder system. Hence this method is apt for producing accurately dimensioned castings. Our well thought-out deliberations in the subsequent write up entail the numerous effects of variation of resin and acid catalyst on the surface defect i.e. sulfur diffusion on the surface of FNB casting. Furan resin; used in the production of casting is furfuryl alcohol and acid catalyst is sulphonic acid. Sulfur diffusion is tested by Energy-dispersive X-ray spectroscopy (EDX) analysis and also by the spectrometer with jet stream technology. This paper also comprises economic advantages of optimizing resin because furan resin is expensive and catalyst with reduction of sulfur diffusion defect as it saves machining, labor cost, and energy.

Keywords: No-bake, Mould-metal interface, Step cone

1. Introduction

Resembling the chemistry of Phenol (C_6H_5OH) and Urea $\{(NH_2)_2C=O)\}$, the furfuryl alcohol ($C_4H_3OCH_2OH$) which is a product of agricultural derivation is able of polymerization with formaldehyde (HCHO) under appropriate pH environment. Though, functional polymers, for no-bake for foundry applications are obtained only when it is accompanied by condensations with Urea, Phenol or both. “The series of resins obtained, having furan ring (C_4H_4O) in chains, at different pH conditions and varying compositions are called Furan resins.”

These resins (binders) and acids (catalysts) make a self-set system, two-part no-bake (universally known as FNB in foundry terms) like alkaline phenolic no-bake (APNB), phenolic no-bake (PNB), alkyd, polyurethane no-bake (PUNB) for binding sand particles for making moulds and cores in foundries. Other primitive binders like molasses, cement, and many proprietary binders have largely been replaced by modern organic binders mentioned above, which meet needs of the rapid production cycle and hence faster production, improved out of the box and handling strength of moulds and cores enhanced de-coring property and eventually better casting finish.

The surface finish of FNB casting is superior due to the higher strengths of the mould which resists defects on pouring of hot molten metal due to which the mould may break out [1]. The amount of furan resin used is usually 0.6% to 1.2% based on sand. Acid Catalyst levels are generally 20% to 60% based on the binder. Furfuryl alcohol is the essential raw material and formerly used resin in FNB casting system [2].

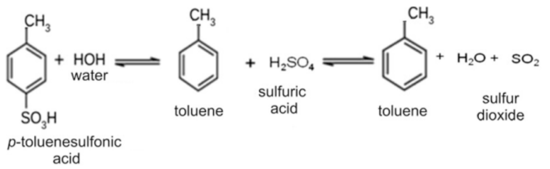
The quality of the cast products produced using FNB system primarily depends on the properties of the mould, specifically strength i.e. compression, shear, tensile and permeability, which in succession depends on the process parameters, such as a number of strokes of ramming, curing time, amount of resin, and amount of hardener. The relationships of these input parameters with the properties of the mould are complex in nature [3].

The binder and catalyst start to react as soon as they are mixed, and having a limited ‘work time' or ‘bench life' during the stage the mould or core must be formed. The final strengths of the mould will be reduced drastically if the work time is exceeded. The work time is normally about one-third of the ‘strip time' and the type of catalyst and its addition rate can control it. The selection of the work time and strip time is based on the capacity of the sand mixer, type and size of the moulds and cores being made, and the time permissible before the patterns are to be reused [4].

The amount of binder higher than the specification level decided by the supplier possibly will cause reduced core strength and casting failure. The probable reason is the increase in the quantity of binder may result in the larger volume of gas generated by the mould. The quantity of binder required increases with finer sand, thereby obtaining a good surface finish [5].

Whenever resin is adding with the catalyst will result in exothermic polycondensation, which is leading to hardening action. The reaction will produce water, which will retard the curing rate (dehydration). The chain forming cross-linking action called further polymerization is the result of the bond producing reaction. The quantity of acid as a hardener in a two-part system can be formulated with well-controlled curing time. The decomposition due to the thermal effect caused by high-temperature liquid metal pouring happens when conventional sulfonic acid with toluenesulfonic acid is used as a hardener [20].

The resulting SO_2 adsorbs on the surface of the liquid metal, and finally decomposes to provide a sulfur atom as shown in Equation (1) and (2).



(1)

$$SO_{2\,(g)} = S + 2O \tag{2}$$

The diffused Sulfur in liquid metal cause sulfidation of the casting surface layer. Sulfur may come in into a reaction with Mn, Fe, Mg to form low melting point sulfides of the S type (Fe, Mn, Mg).

When the reclaimed sand is used, the degenerated nodular graphite can appear in light photographs of casting micro-structure. This happening is much noticeable at the 0.18 % sulfur content in moulding sand Fig. 1 [6,7].

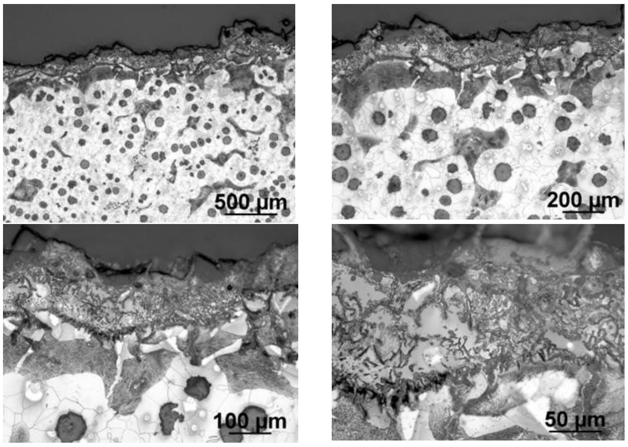


Fig. 1. Surface layer casting microstructure with light photographs prepared with reclaimed sand, sulfur content 0.18% [6,7]

In the production of the spheroidal graphite cast iron prepared with no-bake mould especially furan sand, infrequently the spheroidal graphite degeneration into flaked graphite is observed at the mould-metal interface. This may be the result of the sulfur diffusion from the mould to the metal. This action will result in declining the efficiency of modifier – magnesium. Instead of formation of spheroidal graphite, magnesium will combine with sulfur and form magnesium sulfides. In furan no-bake casting, mould will gain required strength with hardener generally sulphonic acids, sulphuric or phosphoric acid. Very often the sulfur percentage in the reclaimed sand is excessive than desired [8].

The decomposition of the hardener results in the formation of sulfur dioxides as a product as shown in equation (3).

$$C_7H_7SO_3H \rightarrow C_7H_7OH + SO_2 \tag{3}$$

When liquid metal is poured this oxide appears to shift from mould to the casting surface and combined with magnesium as shown in equation (4)

$$SO_2 + Mg \rightarrow MgS + O_2 \tag{4}$$

The reduced concentration of magnesium in the casting surface area leads to graphite degradation and formation of flaked graphite, which will in turn leading to initialization crack formation.

In most of the cases- casting retains of as-cast surface and the mechanical properties are considerably lower than standard ASTM machined specimen. After reviewing the current perspective magnesium diffusion theorem is proposed for compacted graphite iron with consideration of natural convection during solidification [9].

Quality of casting is mainly depending on the main ingredient sand, its contamination with the acid in the case of usage of reclaimed sand - acid demand value (on the basis of pH value), loss on ignition (LoI), grain fineness number (GFN), % of resin etc. For those different variables, effects are evaluated for the sand inclusion defect [10]. This has endowed the researcher with a comparative solution regarding the compressive strength of the mould. Researchers inferred that defects arising due to lower strength of mould can be reduced by variation of resin and hardener as per requirement for the strength [11].

Selection of the proper resin as a binding agent for moulding sands must be preceded by the economic analysis of costs of resins and hardeners. The selection of appropriate resin ought to be carried out on the basis of costs of resins and hardeners. Moreover, selection should be done on the basis of technological needs and produced casting weights [12]. Studies also show that sulfur produces benefits like an improved response to inoculation, increased cell count, and increased strength. From the literature, it has been found that with the increase in sulfur and manganese content the tensile properties improved up to a certain extent and then diminishes. The data of analysis dictate that considerable decrease in strength is observed at the composition higher than the solubility limit of Manganese sulphides [13].

Sulfur from the PTSA (P- p-toluenesulfonic acid) is one of the cause for graphite degeneration at the metal-mould interface and investigated that the sulfur content should be well below of 0.15% in the mould (or even less than 0.07%) to reduce the surface layer depth. The degenerated graphite layers (up to 3.0 mm thick) include a mixture of various graphite morphologies. Generally, transitions from fine lamellar through vermicular to nodular graphite morphologies are noticeable [14,15].

2. Experimental Work

Experiments were performed at the industry producing motor body of gray cast iron (ASTM A48). As a no-bake study, FNB mould system was used to prepare the grey cast iron electric motor body. In the experiments; furfuryl alcohol is used as a resin (binder) and sulphonic acid as acid catalyst. The gating system for the motor body for hot spot and the early freezing area has been optimized in the earlier own research [21].The scanning electron microscopy (SEM) of the sand near the molten metal interface after pouring shows the bonding action as shown in Fig. 2. During experimentation average pH value is close to 4, showing acidic nature of the sand and represent negative acid demand value. The topology of sand and sand size is a critical factor for sand quality analysis. For that test was performed on sieve shaker for grain size distribution. The tests were performed a number of times and in all the cases grain fineness number value (GFN) found close to 48 – showing a good distribution of the sand as per ASTM. The range of selected variables is chosen as per the expert's opinions of industrial personnel and resin suppliers. The % resin is given on base on quartz sand weight and catalyst base on resin weight. Fig. 2 shows the SEM image of sand bonding at 0.80% resin and 35% catalyst (i.e. for 100 kg quartz sand weight, 100*0.8% = 0.8 kg resin and 0.8*35 = 0.28 kg catalyst) near mould-metal interface at 250x and 500x. The mixing of sand, resin, and catalyst is prepared using an automatic sand mixture.

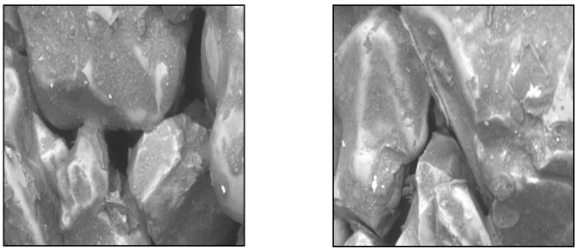

At 250x At 500x

Fig. 2. SEM image of sand bonding at 0.80% resin and 35% catalyst near the mould-metal interface

Table 1 shows the selected variables with its minimum, moderate and maximum level for the experimental investigation. The samples were prepared by variation of resin % based on sand (BOS) and variation of acid catalyst % based on resin (BOR). Three input parameters were selected i.e.: resin%, acid catalyst% and work time, three levels of each parameter were selected based on industrial expert guidance and research support. The value of % resin and % acid catalyst is fixed in automatic sand mixture with a required proportion. The work time is calculated as per the standard test procedure and standard test specimens as per AFS 3180-13-S. The specimens for the compressive, tensile and transverse test are shown in Fig. 3. The related scratch hardness test on a standard mould specimen for the work time calculation is shown in Fig. 4.

Table 1.
Process Parameters and their chosen levels

Sr. No.	Parameter	Levels		
		Low (-1)	Medium (0)	High (+1)
1	% Resin in g	0.70	0.80	0.90
2	% Acid Catalyst in g	35	45	55
3	Work Time (minutes)	5	7	9

Fig. 3. Compressive, tensile and transverse test specimens

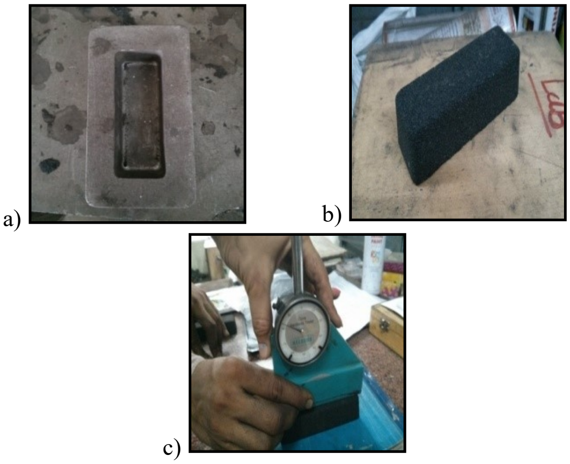


Fig. 4. Scratch hardness test: a) Mould for test, b) Test-specimen, c) Scratch hardness test

Total for 3 variables and 3 levels: $3^3 = 27$ experiments are needed to be performed as per DoE in Minitab software. The experiments were performed for output variables; compressive, transverse and tensile strength for casting surface of better macroscopy and metallurgy. The experiments to check the physical properties of the mould were performed as per AFS 3301-08-S (for tensile strength) and AFS-3306-11-S (for transverse strength). The parameters like flow rate, pouring time, molten metal were kept constant as we undertook in the actual experiment for the study to be performed in industry.

The experiments are performed multiple times for accurate results and their confirmations to know the effects of variation of resin and catalyst on the strength of FNB mould system. The strength of mould is directly connected to the productivity of the casting process considering Rejection rate and consumption of binder. The silica sand is used as moulding sand with composition as shown in Table 2. Table 3 shows the experimental data for the said input-output variables.

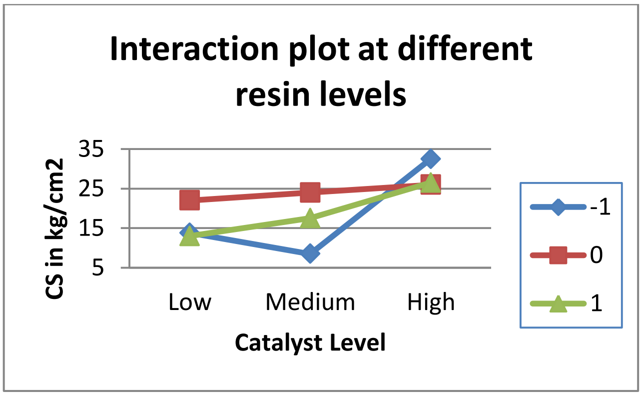
Table 2.
Composition of Moulding Sand [16,17,22]

Constituent	Value (%)
Al_2O_3	1.18
C	6.2-10.24
CaO	0.15
Cl	0.007
Fe_2O_3	1.12
K_2O	0.19
MgO	0.08
Na_2O	0.11
SiO_2	82.70
SO_3	1.13
ZrO_2	0.078
Total	93.0-97.05

Table 3.
Experimental Data for the strength of the mould in coded form for input variables

Sr. No.	% Resin	% Acid Catalyst	Work Time (minutes)	CS $\frac{kg}{cm^2}$	TRS $\frac{kg}{cm^2}$	TS $\frac{kg}{cm^2}$
1	-1	0	0	9.57	6.00	3.60
2	-1	-1	0	11.10	6.00	10.00
3	-1	-1	1	18.11	5.00	5.60
4	-1	1	1	32.00	6.00	5.40
5	0	0	1	16.96	8.50	5.50
6	-1	1	0	33.26	6.00	5.40
7	1	0	0	17.00	6.00	4.10
8	1	0	-1	21.34	2.10	4.60
9	0	0	-1	36.01	6.00	7.00
10	1	1	1	33.62	8.80	10.91
11	1	-1	1	12.40	10.00	9.00
12	0	-1	0	22.00	6.00	8.00
13	1	1	0	9.42	3.00	1.90
14	-1	1	-1	32.00	6.00	5.00
15	0	0	0	18.00	9.50	4.60
16	0	1	1	16.00	1.20	2.30
17	1	0	1	14.00	11.50	3.40
18	0	-1	1	22.05	6.00	8.00
19	**0**	**-1**	**-1**	**21.85**	**5.60**	**3.90**
20	-1	0	1	8.00	4.00	3.00
21	1	-1	-1	10.44	12.50	9.70
22	-1	-1	-1	11.00	6.00	6.90
23	0	1	-1	15.38	1.20	2.50
24	0	1	0	48.00	4.00	5.80
25	-1	0	-1	7.79	4.00	3.00
26	1	1	-1	37.44	1.80	8.81
27	1	-1	0	14.26	12.50	9.70

Here, Work time in minutes
CS = Compressive Strength in kg/cm^2 (15 to 25 kg/cm^2)
TRS = Transverse Strength in kg/cm^2 (4.80 to 9.00 kg/cm^2)
TS = Tensile Strength in kg/cm^2 (2.70 to 5.40 kg/cm^2)



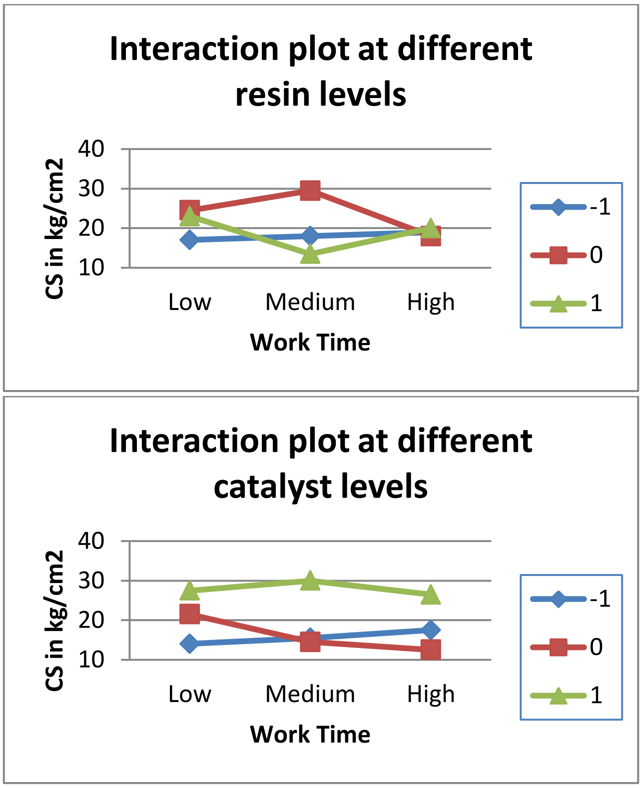


Fig. 5. Interaction plot for compressive strength

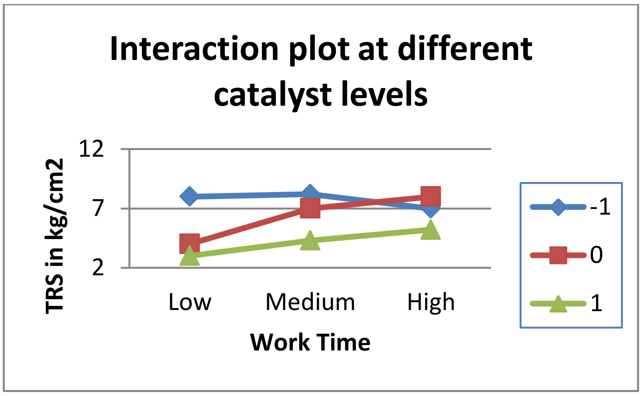
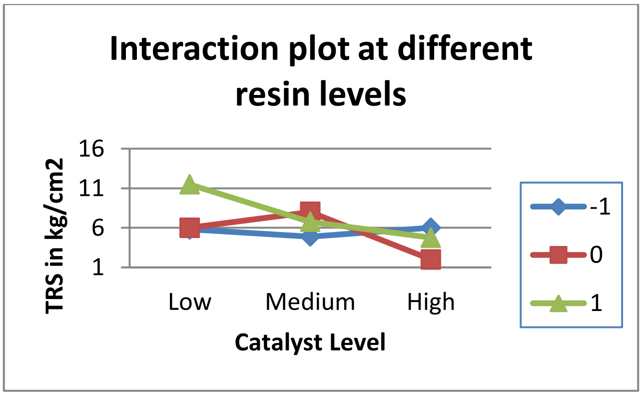
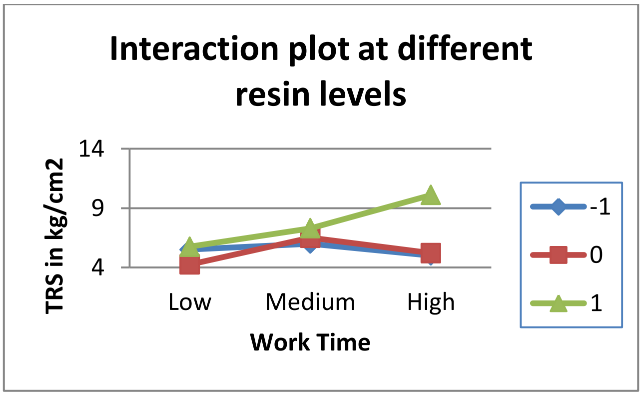


Fig. 6. Interaction plot for transverse strength





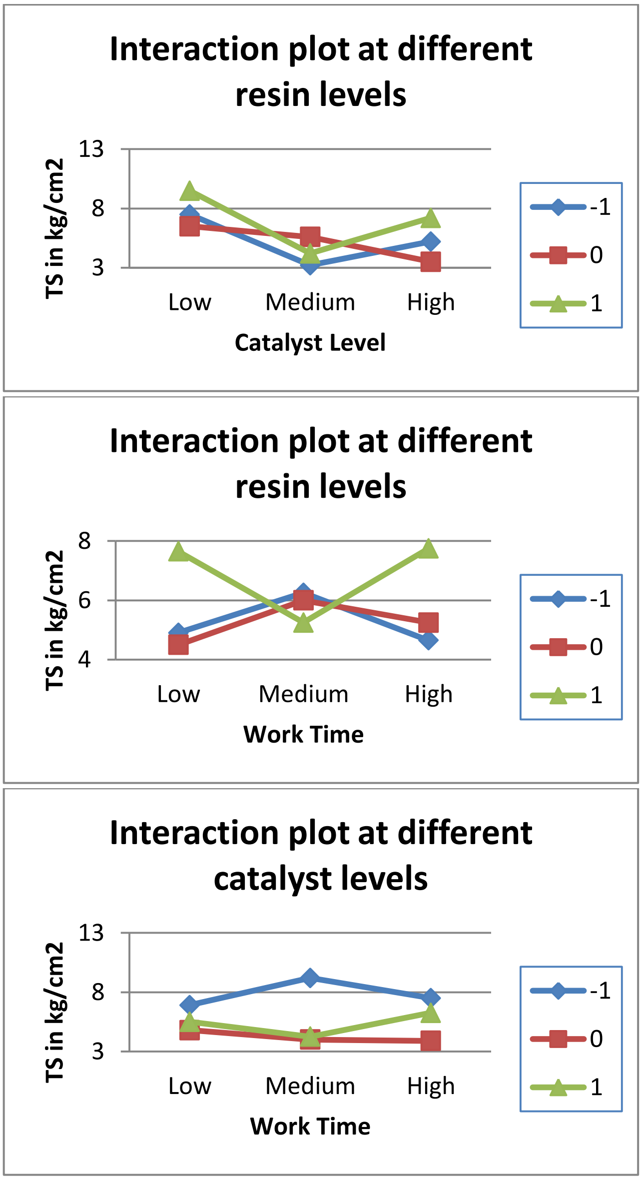


Fig. 7. Interaction plot for tensile strength

3. Interpretation of Interaction plots:

From the Fig. 5-7, the requisite range of compressive strength, tensile strength, and transverse strength are fulfilled at two combinations of resin, catalyst and work time. The two selected optimum parameters combinations are % resin, % acid catalyst and work times are 0.90, 45, 7 and 0.80, 35 and 5 respectively. Out of them, the 0.90% resin is the higher consumption of resin, so it is not very economical; also the 45 % catalyst consumption and 7 minutes work time values are also elevated which are non-optimum in terms of energy and cost-effectiveness. Consequently, we can say that the optimum value of resin, acid catalyst and work time are 0.80%, 35%, and 5 minutes respectively that is optimal in terms of economy, energy, and production sequence.
The bold marked i.e. experiment no. 19 illustrates the optimum values of % resin, % acid catalyst and work time that confers the anticipated results of tensile strength, compressive strength and transverse strength of FNB mould system.
The range of strengths is taken as per industrial and resin supplier's data. The optimum values of the parameters i.e. % resin, % acid catalyst and work time are given in Table 4.

Table 4.
Optimum Values of Parameters

% Resin (Based on Sand)	% Acid Catalyst (Based on Resin)	Work time (minutes)
0.80	35	5

From the optimum values of % Resin, % acid catalyst and work time, FNB mould for the step cone casting is prepared. The step cone is a cylindrical, casting, with a 5 inches (127 mm) external diameter and a height of 7 inches (177.8 mm). The steps within the test casting simulate a wide range of casting sizes and sand-to-weight ratios. Even this design easily lent itself to the study of section size, re-entrant angle (hot spot) and other geometric effects [18].
To prepare a step cone casting the mixture of resin-catalyst-sand was instantly hand rammed into the mould box and the stepped-cone mould was worked with required work time. To produce a completely cured core, the water generated during the reaction needs to diffuse from the interior of the core to the outside of the core. For that, the prepared mould is painted using graphite paint and burnt to extract the amount of moisture. A prepared mould is then poured with gray irons at 1428° C (2600-2610°F) as per the industrial need. Fig. 8 shows the complete procedure related to the preparation of step cone. Four repetitions of the mould have been taken for validation of the result.

a) b)

c) d)

Fig. 8. a) Step cone casting core, b) Complete mould for step cone, c) Pouring of molten metal, d) Step cone casting section for testing

4. Results and Discussions

As we aimed at reduction of sulfur diffusion, we analyzed the content of sulfur in defective FNB casting and also on regularly produced castings. The maximum content of sulfur in grey iron casting should be 0.15% [18]. We performed EDX analysis on defective casting to evaluate the content of sulfur in it. We got the sulfur content value as high as 2.66% on the surface of defective casting which is very much beyond the permissible limit. The energy dispersive spectroscopy readings for the defective casting is shown in Table 5.

Table 5.
EDX Analysis

Element	Weight%	Atomic%
C	40.27	59.76
O	23.15	25.80
Al	3.15	2.08
Si	3.21	2.04
S	2.66	1.48
Ca	0.40	0.18
Mn	0.93	0.30
Fe	26.22	8.37

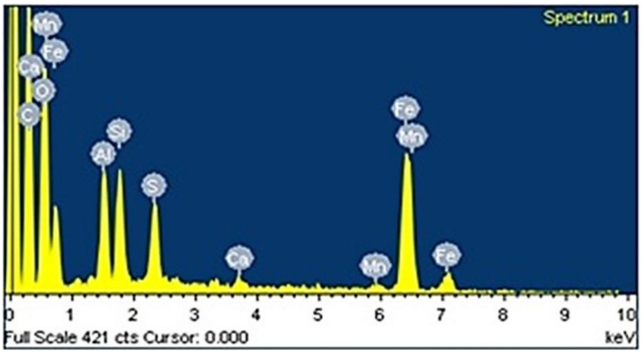


Fig. 9. EDX Analysis of Defective casting

Fig. 9 shows the EDX analysis of defective FNB casting. Here we can see the presence of Mn, Ca, Fe, O, C, Al, Si and S. Furthermore we have evaluated the sulfur content in regular casting before optimization of resin and acid catalyst by chemical analysis through spectrometer which is also 0.18% not within prescribed limit and may show it's adverse effect in future during the service.

We further measured the sulfur content in regular casting after optimization of the amount of resin and acid catalyst and work time through chemical analysis by the spectrometer which gives the sulfur content of 0.12 %. This value is within the permissible range IS 210: Grey Iron Specifications [18].

The experimental work related to the evaluation of sulfur diffusion is fairly imperative for the grey iron casting quality. A higher percentage of sulfur produces ill effects on the quality of the cast iron product. To control the sulfur diffusion on the mould metal interface the resin and catalyst quantities plays a very vital role.

Optimization of % resin and % acid catalyst controls the % of sulfur at mould metal interface. Optimized values of % resin and % acid catalyst are displayed in Table 6. The values favor low consumption of resin (binder) lead to cost-effectiveness as well less fumes (less environmental pollution) are produced due to contact with high-temperature molten metal with less defective pieces (higher productivity).

On the basis of experimental evidence and logic, it can be said that the setting gives the desired results as the moderate level of % resin and lowest value of the catalyst will be required to achieve required strengths against the negative acid demand value of the reclaimed sand. The chosen work time will also put their positive impact on the end result.

5. Conclusion

Maximum sulfur percentage at mould metal interface was 2.66 weight% in defective casting and 0.18 % in the regular casting which is also beyond the limit. It was obtained at the defective casting surface as per data obtained in EDX analysis in figure 5.

It is concluded that applying optimum % of resin based on sand and % acid catalyst based on the binder and the work time lead to weight % of sulfur at mould metal interface reaches to 0.12% which is acceptable [18].

Use of optimum % of furan binder is recommended for better control of sulfur. Better sulfur control is obtained at the combination of parameters given below in Table 6.

Table 6.
Optimum Values of Parameters and the output strengths

% Resin	% Acid Catalyst	Work time (minutes)	CS $\frac{kg}{cm^2}$	TRS $\frac{kg}{cm^2}$	TS $\frac{kg}{cm^2}$
0.80	35	5	21.85	5.60	3.90

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