Evaluation of Rho Alumina Binder on Setting Behaviour Due to Soda Additives and Retarder

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Abstract

Rho alumina is a vacuum produced phase. It is substantially amorphous, and the surface area is around 200 m^2/g. Rho alumina reacts with water at room temperatures and hardens. Because of this bonding property of Rho alumina, in presence of water, this product is widely used as a replacement of cement bond in castables. Usage of alumina binder improves the high temperatures properties of the castables. It also improves the flow properties of the castable mix. Hence it is mostly preferred for the manufacture of No cement castable (NCC), Ultra Low Cement Castable (ULCC), especially where self-flow or pumpable properties are required. Since this is hygroscopic material, it absorbs moisture from atmosphere leading to the deterioration of setting property. In the present investigation an attempt has been made to determine the shelf life of the Rho alumina by evaluating the change in the basic properties of this material like LOI, SSA and XRD phases with the passage of time. An attempt has also been made to find a suitable retarder (with dosages from 0.05 % to 1 %) soda additive and its dosage to obtain desired setting time of this binder. Retarder additive A1 has no effect on the setting time, A2 exhibits increases is setting time at 1 % level. Retarder A3 appears to be a good retarder for this system.

Keywords: Alumina Binder, Hydratable Alumina, Retarder, Setting time, Shelf Life.

1. Introduction

Primarily Rho alumina is a vacuum produced phase [1]. It is substantially amorphous, as its X-Ray pattern shows only a few diffused bands. Its surface area is normally ≥ 200 m^2/g and micropores are not accessible to nitrogen. Rehydration of this material by water at 25°C gives very pure bayerite. It can be produced either by thermal dehydration of gibbsite at 600 °C in vacuum or by flash dehydration of gibbsite by a short time contact with hot air blast at 600 to 900 °C [2]. Rho alumina reacts with water at room temperatures and hardens by the process described by the following equation.

$$\rho Al_2O_3 + H_2O \rightarrow \underset{\text{(Bayerite)}}{Al_2O_3.3H_2O} + \underset{\text{(Boehmite gel)}}{Al_2O_3.1-2H_2O} \quad (1)$$

Because of this bonding property of Rho alumina, in presence of water, this product is widely used as a replacement of cement bond in castables. Usage of alumina binder improves the high temperature properties of the castables. It also improves the flow properties of the castable mix. Hence it is mostly preferred for the manufacture of No Cement Castable (NCC), Ultra Low Cement Castable (ULCC), especially where self-flow or pumpable properties are required.

Prior to 1996 this product was commercially available with Almatis (Alphabond) and Alteo (Actibond). Considering the increasing acceptance of this product by refractory industries, Hindalco developed the material (RH01) and decided to enter commercial market. Since literature on Rho alumina is limited and its production process as well as techniques of evaluation are patented, very little information is available on its basic properties, like shelf life, consistency (water requirement), setting time, etc. Hence Hindalco felt the necessity of generating basic data on this material to provide application support to its customers.

In the present investigation, an attempt was made to determine the shelf life of RH01 by evaluating the change in the basic properties of this material over time. Attempt has also been made to find a suitable retarder and its dosage to delay the setting time of this alumina binder.

2. Materials Used

The physical and chemical properties of RH01 used for the study are presented in Table 1. The calcination of this material was done in BRDC Pilot Flash Calciner (PFC) and milled in pilot ball mill as per the conditions mentioned in Section 3.1. Like other hydratable alumina binder [3], the material has high SSA (196 m^2/g) as well as high LOI (8.2 %). As usual the soda content of this material is also high (Table 1). The Sedigraph analysis shows a wide particle size distribution (Figure 1) with a d_{50} of 3.8 µm.

Table 1. Analyses of the RH01 used for the study.

Properties	Units	Values
XRD		Amorphous (Trace gibbsite)
SSA*	m^2/g	196
LOI	%	8.2
d_{50}	µm	3.8
Consistency	%	36
Initial Setting Time	min	5.5
Final Setting Time	min	9.5
SiO_2	%	0.014
Fe_2O_3	%	0.013
Na_2O	%	0.62
CaO	%	0.026

** Degassing temperature: 300 °C*

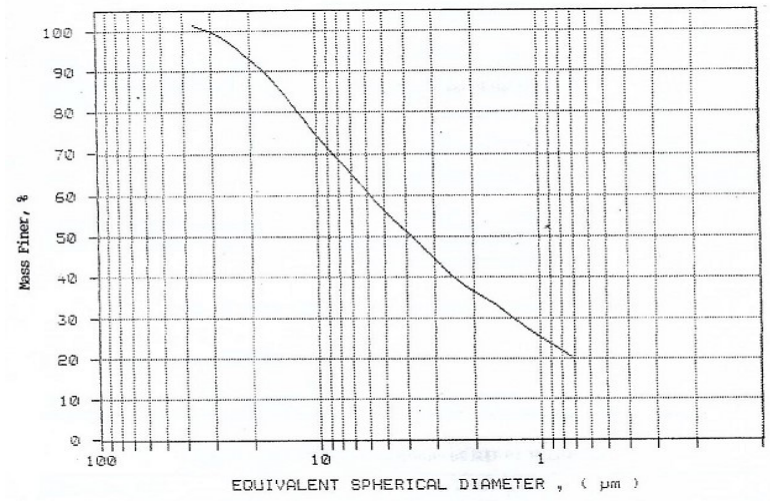

Figure 1. Particle size distribution of RH01 used for the study.

3. Experimental Details

The general flow sheet for the preparation and characterization of RH01 has been presented in Figure 2. The details of the experiments conducted for this study have been narrated in the following sections.

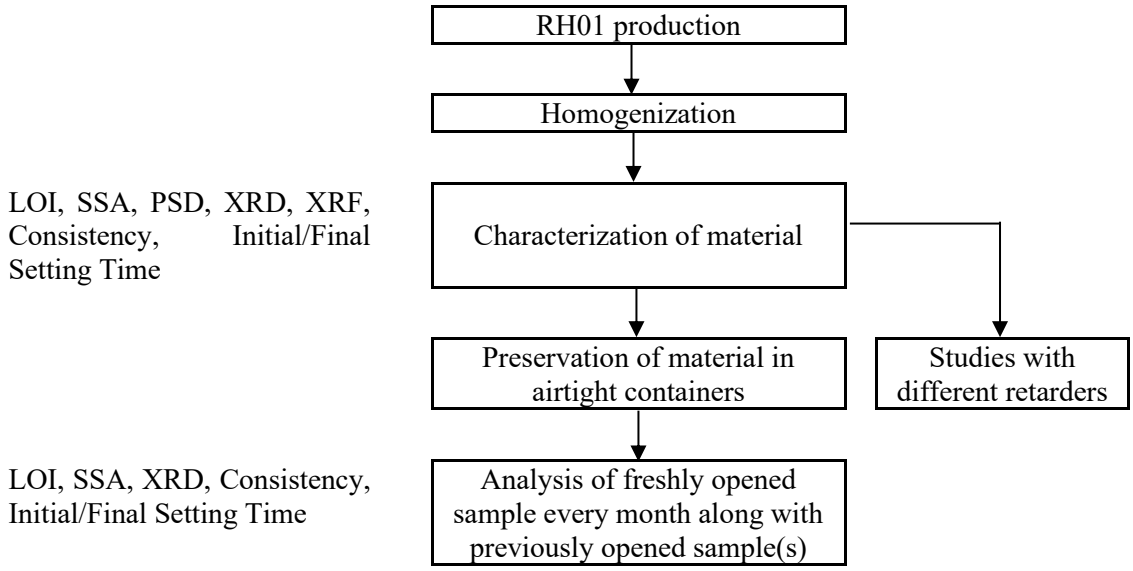

Figure 2. Flow sheet for the application studies of RH01.

3.1 Production of RH01

The feedstock of RH01 was produced following the process conditions mentioned in an earlier report [4]. This was milled in pilot ball mill with dispersing agent and Sodium compound to produce RH01.

3.2 Homogenization and Sampling

Around 80 kg RH01 was produced with desired properties (Table 1) and the material was homogenized in a 120 L plastic drum which was rotated on the ground for about one hour with about 1 kg alumina balls. After this homogenization process the material was removed from the drum and kept in twelve plastic containers (numbered 1–12) in such a way that 1 kg material was stored in container No. 1, 2 kg was stored in container No. 2 and so on. One representative sample was also analysed for different properties (Table 1) to know the initial properties of the material.

3.3 Shelf-Life Determination

RH01 reacts with water and forms hydrous bond. This bonding/setting property is of primary importance for castable manufacturers. Since this is a hygroscopic material, it absorbs moisture from atmosphere leading to the deterioration of setting property. Hence, the preservation period i.e. shelf life of this material needs to be clearly determined. This was determined by conducting the following tests.

The seal of one container was opened in each month and the analysis were conducted along with the samples whose seals were opened in the previous months. The analysis includes the measurement of LOI, SSA, XRD phases, Consistency (IS-4031, Part 4) and Setting Time (IS-4031, Part 5). This practice was continued up to 12 months.

Further, to know the effect of monsoon on the properties of these types of hygroscopic material, one sample was produced in monsoon season and similar type of analysis were conducted every month. This type of analysis was also conducted for another sample, which was purposely kept open in the atmosphere. This was mainly conducted to ascertain the severe effect of surrounding atmosphere on the shelf life of the material.

3.4 Effect of Additives on Setting Times

Since the initial setting time of 'as is' material is very low (5.5 minutes in present case), difficulties may arise in working with this material. Hence a study was conducted to find out a suitable additive (retarder) and its dosage to increase the setting times of this material.

4. Results

The results of the study are presented in the following sections.

4.1 Shelf Life

The results of the analyses on LOI, SSA, Initial and Final Setting Time are presented in Tables 2 to 5 and Figures 3 to 6. It can be seen from Table 1 that the starting material (RH01) contains trace level of gibbsite, and this same level of gibbsite is observed in all the samples analysed throughout the period. Hence, only typical XRD plot of all the twelve samples which is given in Figure 7. It is known that the consistency (water requirement) has a direct relation with the setting times of this material. Hence, same consistency (as measured in 'as is' material, Table 1) is maintained throughout the study.

From Table 2 and Figure 3, it is observed that there is no significant change in LOI in the initial six months period. Slight increase in LOI is observed in July and August months. This is probably because of monsoon. Afterwards, again November and December months' results show slight increase in values. However, results show slight change (decrease) in December only (Table 4 and Figure 4). Although both the initial and final setting time (Tables 4 and 5) exhibit similar trend like LOI, the increase in values in November and December months is found to be considerably higher (Figures 5 and 6). In general, it can be said that there is no deterioration in the properties of RH01, up to six months after the production.

Table 2. LOI of RH01 stored for different time periods.

Sample → / Month ↓	0	1	2	3	4	5	6	7	8	9	10	11	12
0	8.2												
1		8.29											
2		8.24	8.15										
3		8.68	8.51	8.62									
4		8.29	8.22	8.52	8.36								
5		8.3	8.03	8.16	8.28	8.39							
6		8.23	8.4	8.33	8.64	8.58	8.69						
7		8.7	8.43	8.43	8.71	8.77	8.62	8.73					
8		8.71	8.59	8.72	9.03	8.96	8.98	9.09	8.92				
9		8.76	8.54	8.6	8.89	9.01	8.8	8.98	8.86	8.81			
10		8.66	8.56	8.57	9.04	9.17	8.75	9.06	9.02	8.9	8.72		
11		9	8.89	8.94	9.31	9.28	9.06	9.2	9.11	8.92	8.88	9.07	
12		8.93	8.74	8.86	9.3	9.05	9.09	9.04	9.18	8.99	9.01	9.18	9.74

Table 3. SSA of RH01 stored for different time periods.

Sample → / Month ↓	0	1	2	3	4	5	6	7	8	9	10	11	12
0	196												
1		192											
2		190	188										
3		191	192	192									
4		193	192	195	193								
5		192	190	188	189	190							
6		194	193	194	192	190	191						
7		191	191	192	186	191	192	185					
8		193	193	195	191	192	192	193	192				
9		191	189	186	189	187	190	190	189	187			
10		190	190	183	190	186	191	192	188	190	188		
11		192	189	189	180	188	191	184	186	190	188	190	
12		185	186	184	183	190	190	185	186	182	182	189	188

Table 4. Initial setting time of RH01 stored for different periods.

Sample → / Month ↓	0	1	2	3	4	5	6	7	8	9	10	11	12
0	5.5												
1		5											
2		5.5	5.5										
3		4.5	4.5	4.5									
4		4.5	4	4	4								
5		4.5	4.5	5	6	5							
6		4.5	5	5	7	5.5	5.5						
7		6.5	6.5	6	8.5	7	6.5	8					
8		6.5	6.5	7.5	10.5	8.5	6.5	8	6.5				
9		6.5	6	6	7.5	7.5	6.5	6.5	6	6			
10		6	6	6	6.5	7.5	6	7	7	7.5	6.5		
11		8.5	8	7.5	9.5	10	7.5	10	9	8	7	7.5	
12		11.5	9.5	10.5	14	13.5	10.5	10.5	11.5	10	8	9.5	15

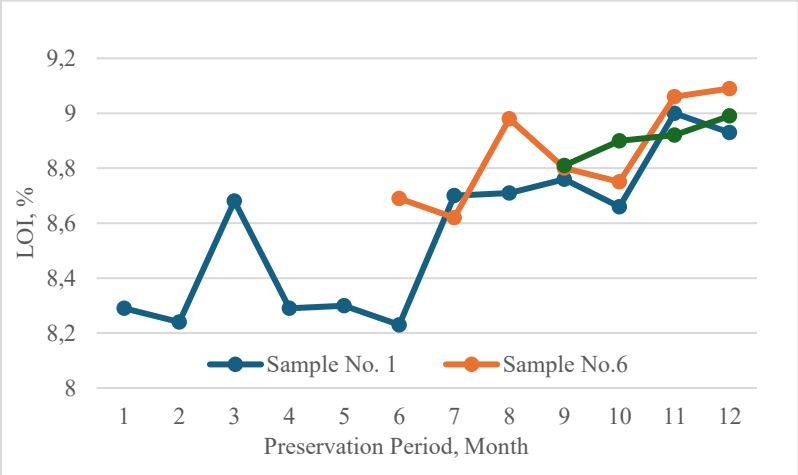

Figure 3. LOI of RH01 stored for different time periods.

Table 5. Final setting time of RH01 stored for different periods.

Sample → / Month ↓	0	1	2	3	4	5	6	7	8	9	10	11	12
0	9.5												
1		8											
2		9	9										
3		8	8	7.5									
4		8	8	7.5	8								
5		8	8	8	9.5	8							
6		8	9	8	11	9	9.5						
7		9.5	10	9.5	12.5	11	11	12					
8		11	10.5	11.5	14.5	12.5	11	12	11				
9		10	9.5	9	11.5	11.5	9.5	9.5	9.5	9.5			
10		9.5	8.5	8.5	10.5	11.5	9.5	11	10.5	10.5	9.5		
11		14	13.5	12.5	14.5	15.5	12.5	15.5	14	12.5	11.5	12	
12		17.5	15.5	17	19	19.5	18	16.5	18	16	13	16	21

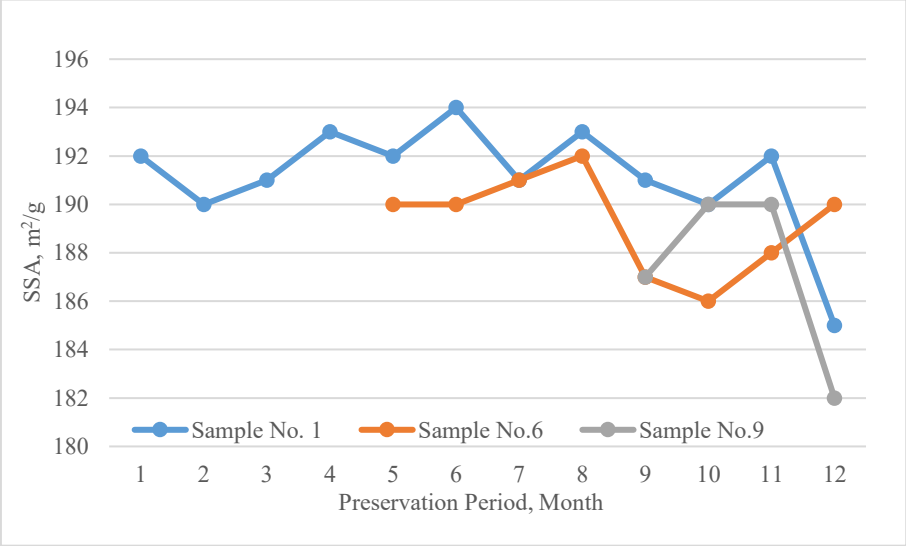

Figure 4. SSA of RH01 stored for different time periods.

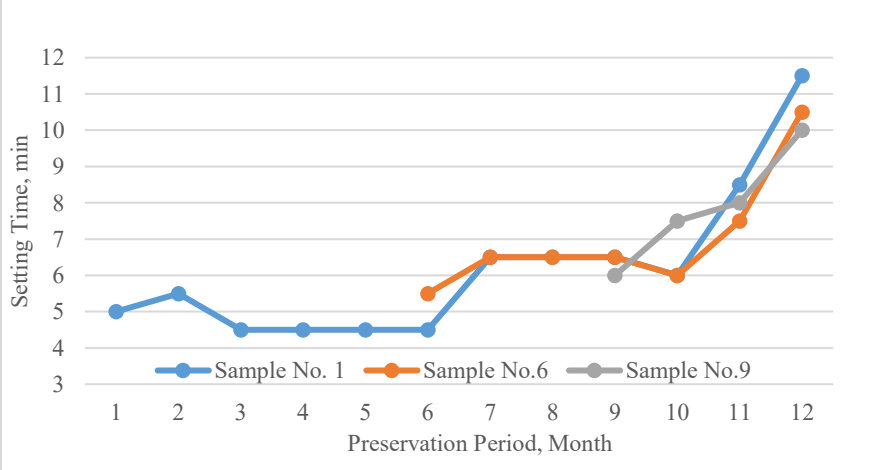

Figure 5. Initial setting of RH01 stored for different time periods.

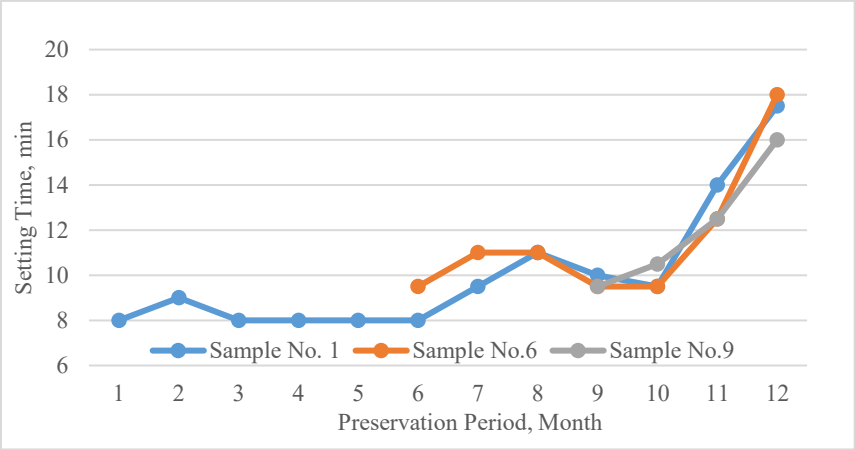

Figure 6. Final setting time of RH01 stored for different time periods.

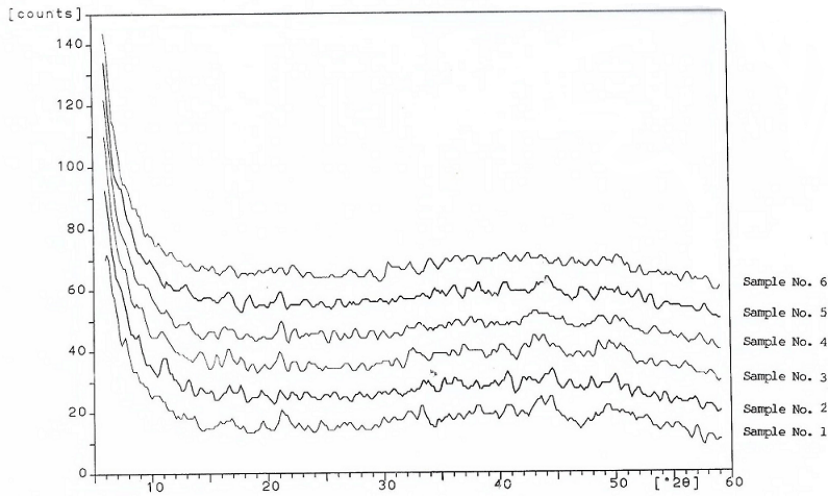

Figure 7. XRD plot of RH01, produced in first month and analysed after 12 months.

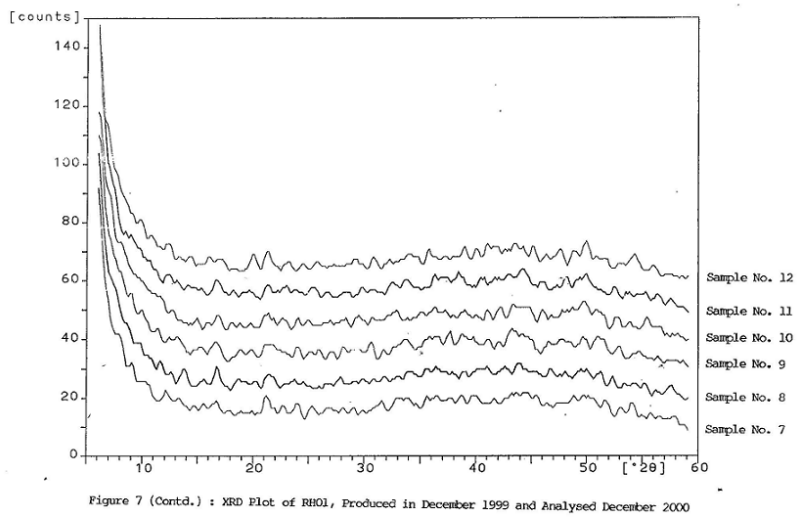

Figure 8. XRD plot of RH01, produced in first month and analysed after 12 months.

However, the material, which was left open in the atmosphere, starts deteriorating from the first month itself (Table 6). A considerable amount of deterioration in all the properties takes place in second month. It fully deteriorates in fourth month exhibiting very poor setting characteristics (final setting > 180 min) of this material.

Table 6. Properties of RH01 kept open in the atmosphere for different periods.

Properties	Initial	After 1 month	After 2 months	After 4 months
LOI, %	8.2	9.04	10.56	18.4
SSA m^2/g	196	185	177	163
XRD	Amorphous	Amorphous	Amorphous	Amorphous
	(Trace gibbsite)	(Trace gibbsite)	(Trace gibbsite)	(Trace gibbsite)
Consistency, %	36	36	36	36
Setting time, min				
Initial	5.5	9	32	> 180
Final	9.5	13	43	

The material produced in monsoon season shows higher LOI value (Table 7) than the material produced in December, although other properties like SSA, Consistency, Initial & Final setting Time and XRD phases are similar. LOI and SSA of this material generally did not change with the passage of time (measured up to sixth month). However, the change (increase) in setting times is very high (Figure 8) compared to the material produced in December (winter). In short, it can be said that the material produced in rainy season should be consumed in the same month. Hence, it is always better not to produce this type of material in the rainy season.

Table 7. Properties of RH01 produced in monsoon season (August).

Properties	Initial	After 1 month	After 2 months	After 3 months	After 4 months	After 5 months	After 6 months
LOI, %	9.22	9.5	9.67	10.02	9.87	9.92	9.62
SSA, m^2/g	196	194	194	189	190	189	195
XRD	Amorph.	Amorph.	Amorph.	Amorph.	Amorph.	Amorph.	Amorph.
	(Trace gibbsite)	(Trace gibbsite)	(Trace gibbsite)	(Trace gibbsite)	(Trace gibbsite)	(Trace gibbsite)	(Trace gibbsite)
Consistency, %	36	36	36	36	36	36	36
Setting Time, min							
Initial	5.5	7.5	10.5	10	14	13	13
Final	8.5	11.5	14	14	21	20	21.5

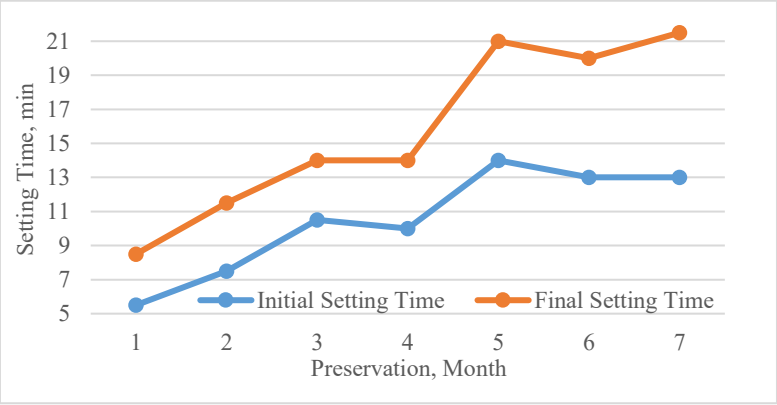

Figure 9. Setting times of RH01 (produced in monsoon season) stored for different time periods.

4.2 Effect of Additives on Setting Times

Studies on the effect of retarders (additives) show that microsilica has no effect on the setting times of this material (Table 8). Although $CaSO_4$ exhibits increase in setting time at 1 % level, it not advisable to use the same because of its negative effect on high temperature properties of the material prepared with this RH01. Citric acid appears to be a good retarder for this system. Since this is a proven material in different type of castable, this can be used for this alumina binder also. However, it is to be used only if the customers find the RH01 binder to be setting very fast in their castable compositions.

Table 8. Effects of retarders on the setting time of RH01

Retarder (%)	Initial	Final
Nil	5.5	9.5
Microsilica (A1)		
0.1	5.5	9.5
0.15	5.5	9.5
0.2	5.5	9.5
1	5	8
$CaSO_4$ (A2)		
0.05	5.5	9.5
0.1	5.5	9.5
1	12.5	16
Citric Acid (A3)		
0.05	5.5	9.5
0.1	6.5	10.5
0.2	7.5	13
0.5	9.5	12.5
1	32	40

5. Conclusions

The RH01 is an alumina binder, and it improves both the flowability and high temperature properties of castable system. It is mostly used in NCC and ULCC applications, especially when self-flow/pumpable properties are required. This is a hygroscopic material and hence it should be always preserved in airtight containers. The evaluation of this material reveals that the original properties remain intact up to six months from the date of production while being periodically opened for use. Alcoa's product information on similar type of binder also suggests 6 months shelf life (Annexure-I). Therefore, same 6 months shelf life for RH01 can also be guaranteed.

The monsoon season has an adverse effect on the properties of this material. Hence, it is not advisable to produce this material in rainy season. Otherwise, it should be consumed within a short period, preferably within one month after production. For some of the applications, where more working time (than the usual) is required, citric acid can be added to retard the setting of this material.

6. References

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