Effect of Diesel Oil , Sodium Oleate and Hydroxyethylcellulose (HEC) as Retarders on Hydration of Lime

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Abstract Effect of various additives on hydration of lime has been carried out. Lime which is formed by the calcining of lime stone (CaCO_3) at 1000°C is of great importance. As, it is used in laboratory as reagent, in the manufacture of bleaching powder, glass & steel making, in agriculture as source of calcium and in water treatment, neutralization of soil acidity etc. More than 72% of lime stone is used in the manufacture of cement. Though free lime does not found in properly made Portland cement (generally found in its hydrated form) but it plays an important role in the setting of cement. Sometimes fast reactivity of lime decreases the strength of set cement due to false setting. By adding certain chemicals (retarders), the hydration of lime can be slowed down and it may help in overall increase in setting time as well as strength of set cement. Various additives –called retarders - are added to inhibit the setting of cement such as gypsum, sucrose etc.

Keywords Diesel Oil , Sodium Oleate , Hydroxyethylcellulose (HEC) , Retarders , Hydration of Lime

1. Introduction

The retarders are of great importance, as it is used in various fields such as in cement industries, corrosion retardation, fire retardation, pollution retardation, soil erosion retardation, acidity of soil retardation, in human health as bacteria retardation etc. This study includes the determination of available lime and the slaking rate of lime in presence of other chemicals. Though this study may not have direct application in cement industries but it may serve a guide for similar reactions where reactivity of lime with water is applied for specific use. This work is aimed to find out a suitable chemicals or additives which can delay the reactivity of lime with water.

General properties of Chemicals used for study:

(i) Diesel oil :

It is a hydrocarbon having carbon atom $\text{C}_{16} - \text{C}_{20}$ and is obtained from an intermediate weight petroleum components having boiling points between kerosene and lubricating oils (i.e. 419-487, Welker 1985). Actually, diesel oil form an emulsion in distinct layer with water. It has ability to suspend the solid particles. It is brown coloured liquid having some smell.

(ii) Sodium Oleate : It is made from oleic acid having molecular formula $\text{C}_{18}\text{H}_{33}\text{O}_2\text{Na}$. Its structural formula is as, (Finar 1973 and Howley 1950) :

(iii) Hydroxyethylcellulose (HEC) :

It is Cellulose ether, formed by the reaction between ethylene oxide and cellulose. Two types of derivatives have been obtained, one is water soluble and other is alkali soluble. The main uses of water soluble derivatives are based on non-ionic character, resistance to heat getting. Application includes pigment carrier in printing pastes, protective colloids in electroplating and binder in ceramic (Snell et al, 1977).

While alkali soluble type of HEC is used for making extruded film which has exceptional dimensional stability, sparkle and clarity. It is used in certain textile sieving and finishing treatments.

3. Experimental

a) Determination of Slaking Rate:

Fig. 3-1 Determination of slaking rate of lime

Slaking rate determines the reactivity of lime. Lime which is completely hydrolysed within 5 - 10 minutes is called highly reactive and hydrolysed between 10 - 20 minutes is medium range reactive while hydrolysed after 20 minutes is low reactive.

For determining the slaking rate, 50 mg of lime was added to 50 ml of distilled water taken in a beaker, left it for 5 minutes and then kept in ice to freeze the further reaction. A drop of PR indicator was added to the solution and titrated against EDTA solution maintaining the pH value 10, by adding 1M NaOH. The whole solution was stirred on magnetic stirrer. At the end point colour of the solution changed from pink to clear blue.

Similar experiments were performed at the interval of 10 minutes, 20 minutes, 40 minutes and 1 hour respectively and data were recorded.

After calculation and plotting the graph, it was concluded that most of the 71% available lime (i.e. 68.2%) hydrolysed within 5 minutes and rest (2.7%) completely hydrolysed within 10 minutes shown in fig.3-1.

b) Reaction of Lime in Diesel Oil:

Procedure :

40 mg of lime was added to oil water mixture (5 ml oil – 50 ml water), pH of this solution was measured by pH paper because pH meter was not effective in oil medium and a drop of PR indicator was added to the solution and required volume of EDTA solution was added at a time. The whole solution in a beaker was stirred on a magnetic stirrer. At the end point, colour of the solution changed from pink to blue. pH of the solution at the end point and time required for complete neutralization were measured. Same experiments were done in different proportions or ratio of oil – water mixture. The same observations were made in diesel oil – water (5 : 50) at different temperatures i.e. 40°C and 20°C respectively and the data observed are shown in Table – 1

& fig. 3.5.

Fig. 3.5. Effect of diesel oil on the hydration of time

Result and Discussion

It was found that with increasing the proportion of oil in oil-water mixture, time required for complete neutralization of reaction increases. It indicates that diesel oil delayed the hydration of lime. Thus diesel oil acts as a retarder. But at higher temperature (i.e. 40°C) the reaction is completed within two minutes i.e. the reaction could not be slowed down rather accelerated. At lower temperature i.e. at 20°C reaction freezes.

c) Reaction of lime in sodium oleate solution of different concentrations:

(i) Preparation of 5% sodium oleate solution:

5g sodium oleate was dissolved in 100 ml distilled water. The mixture formed some foams. From this solution 0.01%, 0.1%, 0.5% and 1% solution were prepared by dilution. pH of the different solutions were measured and then used for experiments.

Procedure

40 mg of lime (particles size – less than 75 μm) was added in 25 ml of sodium oleate solution & pH of the solution was measured. A pinch of PR indicator was added to it. The colour of the solution becomes pink. A required volume of EDTA solution was added at a time. The whole solution in a beaker was stirred on a magnetic stirrer. At the end point colour of the solution turned pink to clear blue. pH of the solution at the end point and time required for complete neutralization were measured. Similar experiments were carried out at different concentrations of sodium oleate. Then 0.5% sodium oleate, diesel oil mixture (1 : 1) were used. Observations made are given in Table – 2 and fig.3.2.

Table 1. Effect of Diesel Oil in the Hydration of Lime

Ratio of Diesel Oil : Water in ml.	pH of Diesel oil	pH of solution	pH at end point	% of Lime	Time required for end point	Indi-cator
5 : 50	7	11.0	9.0	71	27 min.	PR
10 : 10		10.0	8.5		29 min.	
15 : 10		10.0	8.0		42 min.	

Table 2. Effect of Sodium Oleate on the Hydration of Lime

% of sodium oleate	pH of sodium oleate solution	pH of Soln. (lime + sod. oleate)	pH at the end point	% of Lime	Time required for end point	Indi-cator
0.01	8.45	11.21	8.35	71	Within 2 min.	PR
0.1	8.27	11.03	8.23	71	2 min.	
0.5	9.58	10.90	8.60	71	4 min.	
1.0	9.72	11.0	10.65	71	10 min.	
5.0	9.42	9.39	lime is not completely dissolved			
0.5 sodium oleate solution + diesel oil (15 : 15)			10.50	71	1 min.	

Table 3. Effect of HEC on Hydration of Lime

% of HEC solution	pH of the HEC soln.	pH of the soln. (lime + HEC)	pH at end point	% of lime	Time required for end point	Indi-cator
0.5	11.35	11.06	11.14	71	1 min.	PR
1.10	11.45	11.08	11.15	71	1 min.	
1% HEC + Diesel Oil (1:1)		10.50	9.00	71	1 min.	

Result and Discussion

From Table 3 and Fig. 3 it is observed that with increasing concentrations of sodium oleate solution, time required for complete neutralization has increased. It indicated that hydration of lime can be delayed by increasing the concentration of sodium oleate solution. But after certain concentration lime was not hydrolysed. It indicates that sodium oleate acts as a reaction retarder. In diesel oil - sodium oleate solution, it acts as reaction accelerator.

Fig. 3-2 Effect of sodium oleate on the hydration of lime

d) Reaction with Hydroxy Ethyl Cellulose(HEC)

1 gm of HEC was dissolved in 100 ml distilled water. Since HEC did not dissolved easily in water therefore 1 or 2 drops of NaOH was added to it. The whole solution in a beaker was stirred on a magnetic stirrer. From this 1% solution, 0.5% solution made by dilution. The pH of solution was measured and then used for the experiment.

Procedure:

40 mg of lime was added to 25 ml of HEC solution. The

pH of this solution was measured. A pinch of PR indicator was added to it. A required amount of EDTA solution was added at a time. The whole solution in a beaker was stirred on a magnetic stirrer. At the end point the colour of the solution turned pink to clear blue. The pH of the neutral solution and the time required for complete neutralization were measured. Similar experiments were done in 1% HEC – diesel oil mixture (1 : 1) and same with 1% HEC solution at 40°C and 20°C. The observed data are shown in Table 3.

Result and Discussion

From Table 3 it is clear that HEC in fact has accelerated the reaction even in diesel oil.

4. Conclusions

In present investigation, effects of different chemicals or additives (retarders) on the reactivity of lime with water were studied. Time required to attain the equilibrium for the reaction between lime and water under various conditions were measured. This was estimated by complex metric titration.

In each case 40 mg of sample was added to 25 ml of solution of desired chemicals. To ignore the effect of low diffusion rate on the reactivity of lime under static condition, the mixture was stirred on a magnetic stirrer constantly. This eliminated the possibility of high concentration of $\text{Ca}(\text{OH})_2$ in the vicinity of solid surface and thereby inhibiting the reaction. Different concentrations of sodium oleate, diesel oil and HEC were taken. The effects of these chemicals (sodium oleate and HEC) were also seen in diesel oil mixture.

It was seen that with 1% sodium oleate solution the reaction between lime and water can be delayed by 10 minutes - 12 minutes. In presence of diesel oil (3:2 ratio of oil-water) reaction was delayed by 40-42 minutes. It was expected that these chemicals form a mechanical barrier

around the solid particles and it can be dispersed. High molecular weight compound might have formed a viscous and strong three dimensional structure in the surface layer that retarded the reaction.

Retardation due to diesel oil might be due to adsorption of diesel oil on the calcium oxide surface. After addition of water, oil layer leads to depletion. It appeared that the reaction can be delayed further by controlling the depletion of oily layer.

After maintaining the temperature of the reaction mixture in one case at 40°C and in another at 20°C, it was observed that at elevated temperature the reaction could not be slowed down. At 20°C, reaction rate was found to have reduced appreciably.

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