Original Research Article

Synthesis and characterizations of sodium gluconate and study of its effects on the properties of Ordinary Portland cement as a retarding admixture

ABSTRACT

The use of retarding admixtures in concrete has been found to enhance the properties of Ordinary Portland Cement (OPC) by delaying the onset of setting and improving the workability of the concrete. This study aimed at synthesizing and characterizing sodium gluconate as a retarding admixture and investigating its effects on the physical and mechanical properties of OPC. Sodium gluconate was synthesized through a simple chemical process involving the reaction of gluconic acid with sodium hydroxide. The synthesized product was characterized using Fourier Transform Infrared (FTIR) and ^{1}H-NMR spectroscopy. The results showed that the synthesized sodium gluconate had a characteristic absorption peak at 3205cm^{-1}. The effects of sodium gluconate on the properties of OPC were studied by incorporating various concentrations of the admixture in the cement mixtures. The variations were investigated for setting time, compressive strength, and porosity. The results showed that the inclusion of sodium gluconate in OPC prolonged the setting time, increased the workability, and reduced the compressive strength. Additionally, the incorporation of sodium gluconate in OPC resulted in a decrease in the water-to-cement ratio, which significantly improved the porosity of the resulting concrete. Based on the results, it can be concluded that sodium gluconate has the potential to be used as a retarding admixture in OPC.

Keywords: Setting time, Sodium gluconate, Retarding admixtures, Ordinary Portland cement.

1. INTRODUCTION

Chemical admixtures have been used for a long time with concrete and possessed a developing field of study. The properties of concrete are altered depending on the proper use of the admixtures. For example, properties such as flow ability, setting time, water absorption, and compressive strength of cement are some parameters that change based on the type and quantity of admixture used. The use of chemical admixtures can be traced back to the Roman era. The Romans would mix a lot of different things into their concrete which would result in changing its strength of it. But the first modern-day use was in 1933 when engineer Bertrand H. Wait started experimenting with different blends of Portland Cement [1]. In the past, concretes with a maximum compressive strength of 30 MPa and a slump of 100mm were used for structures in the US and Canada. But now, these figures have changed to 80-100 MPa concretes with slumps of figures around 200mm for building lower parts of the columns of high-rise buildings [2,3]. Concrete is a composite material for construction composed of cement and other cementitious materials such as fly ash, slag, cement, aggregates (crushed limestone, granite, sand), water, and admixtures [4]. Admixture is defined by ACI 116R-00 as "a material other than water**,** aggregates, hydraulic cement, and fiber reinforcement, used as an ingredient of a cementitious mixture to modify its freshly mixed, setting, or hardened properties and that is added to the batch before or during its mixing activity" [5].

Ordinary Portland Cement (OPC) is commonly used as the binding material for concrete. However, OPC has some limitations, such as fast setting time, low workability, and high heat of hydration, making it difficult to use in large volume construction projects. These limitations can be overcome by using retarding admixtures in cement mixtures. Retarding admixtures are chemical compounds that are added to cement mixtures to delay the setting time and improve the workability of the resulting concrete. The retarding admixtures work by delaying the onset of setting by inhibiting the hydration reaction involving between the cement and water. The retardation of the setting also reduces the peak exothermic heat evolved during cement hydration, reducing the risks of thermal cracking. According to one study, cement fluidity required a certain amount of gluconate to be present after five minutes of hydration [6,7].

Among the different types of retarding admixtures, sodium gluconate has been found to be effective in improving the physical and mechanical properties of OPC. Sodium gluconate is sodium salt of gluconic acid and is a by-product of fermenting glucose with the aid of microorganisms. Sodium gluconate is widely used in the food and pharmaceutical industries as a sequestrant, chelating agent, and buffer. Sodium gluconate has a unique chemical structure, which allows it to interact with calcium ions in the cement, delaying the onset of setting. However, inappropriate use of sodium gluconate frequently results in anomalous setting and significant slump losses, which has a significant negative economic impact.

In this study, our aim was to synthesize and characterize sodium gluconate and investigate its effects on the physical and mechanical properties of OPC.

2. MATERIALS AND METHODS/EXPERIMENT DETAILS/METHODOLOGY

Materials and Methods:

Materials:

The materials used in the study were OPC, fine sand, sodium gluconate, and water. The OPC was obtained from a local supplier and had a fineness of 320 m^2/kg. The fine sand had a fineness modulus of 2.55 and a specific gravity of 2.60. The sodium gluconate was synthesized using gluconic acid and sodium hydroxide. The water used in the study was potable water.

2.1. Experimental:

2.1.1. Synthesis of Gluconic Acid:

50 grams of glucose was dissolved in 100 mL of distilled water in a beaker. A 12% H_2O_2 solution of 78.66 mL was added, which contained 9.44 grams of $H_2O_2$by the molar ratio required. To react with the glucose added earlier. The solution was heated in a water bath at 75-80 degrees Celsius.

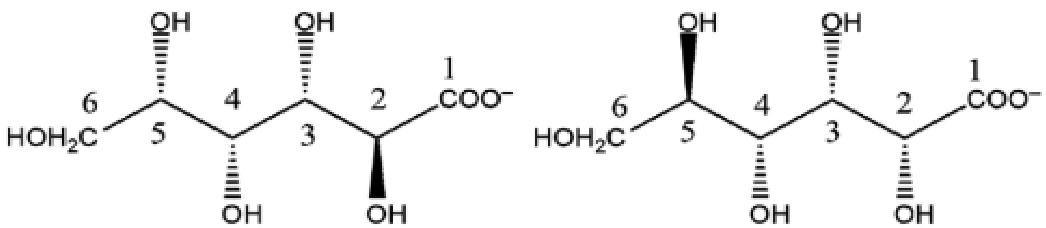

Fig.1. the structure of L-gluconate (left) and D-gluconate (right)

After heating for 60 minutes, the 10 mL solution was separated and cooled to >10 degree Celsius to stop the reaction of the peroxide and glucose, and the pH was measured. This process was continued until a constant pH was attained, and the pH would not lower any longer, indicating the completion of the reaction involved.

The whole solution, which was heated for a total of 75 minutes, was cooled below 10 degrees Celsius to stop the reaction of the excess peroxide if any remaining one. Then the produced super-concentrated solution was left out for crystallization. The grown crystals were hypothesized to be Gluconic Acid (GA). The reaction was done twice to get two samples of gluconic acid precipitates. The percentage of yield was 71.34.

2.1.2. Synthesis of Sodium Gluconate

2.2. Reactants used

The reactants used for the reaction were (1) D-glucose, (2) H_2O_2 (30%) and (3) NaOH.

2.2.1. Reaction conditions

Reaction for gluconic acid was run at 70-80˚Cin a water bath for 70-75 minutes. The temperature was maintained at 55-60˚C for the crystallization of Sodium gluconate. The procedure followed here differs from Mao's procedure in the crystallization technique of gluconic acid. In his paper, he reported separating gluconic acid crystals by freeze-drying. The gluconic acid concentrated liquid solution produced in the lab for this experiment was separated by keeping it out to rest for two to three days.

2.3. Procedure

2.3.1. Preparation of Sodium gluconate from produced Gluconic Acid:

The gluconic acid crystals produced in Reaction-1 were dissolved in 100 mL water, and a 0.05 M NaOH solution was added until the pH of the solution reached at7. The solution was slowly boiled at 50-60˚C to less than one-fifth of the initial volume in a water bath. The crystals of Sodium gluconate precipitated over

3-4 days. During boiling, any change in pH was adjusted by the addition of NaOH. Produced crystals will be referred to as SGA

2.3.2. Yield of sodium gluconate

Yield of sodium gluconate with respect to glucose = (29.398/50) x 100% = 58.79%

2.3.3. Observation from setting time experiments:

Initial and final setting times were determined. It was observed that 1% Sodium gluconate provided a decent prolongation of initial setting time which is just less than double of the blank [8]. We can say that there is more room for improvement of the produced sodium gluconate and that it is not pure as, according to literature, sodium gluconate is more potent as a retarder, and 0.02-0.04% pure sodium gluconate would provide these effects in cement. The compound we synthesized is less potent retarder than pure sodium chloride as it contains specific amounts of gluconic acid and glucose as impurities.

2.4. Results of Compressive Strength Experiments:

Compressive strength: Compressive strength is defined as the ability of a material to resist the direct pressure of applied compression force. Voids and microchannels inside the hydraulic cement provide adequate hydration of the material and subsequently increase its compressive strength [9].

2.4.1. Procedure

The prepared concrete was mixed in a 2x2-inch steel cube mold for casting. Once, it was set after 24 hours, the concrete cube was removed from the mold. The test specimens were submerged underwater for a stipulated time. As mentioned, the specimen must be kept in water for 3 or 7 or 28 days, and at every 7 days the water was changed. The concrete specimen was well-dried before placing it on the hydraulic press. Testing specimens were placed in the space between bearing surfaces. The concrete cubes were placed on the bearing plate and appropriately aligned with the center of thrust in the testing machine plates. The loading was applied axially on the specimen without shock and increased until the specimen collapsed. Due to the constant application of load, the specimen starts cracking at a point and final breakdown of the specimen was noted, which is the compressive strength for that particular block in a specific time.

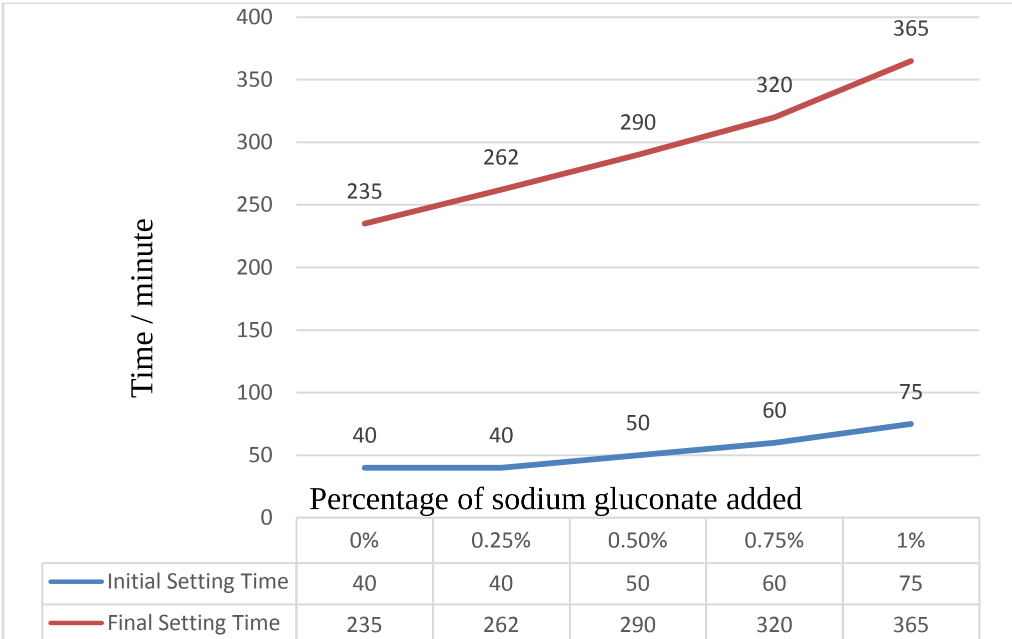

Fig. 2.Initial and final setting time of sodium gluconate mixed with CM-1 at different weight percentages of cement

2.4.2. Experimental Data

Compressive strength is observed at intervals like 3, 7, 28 days, and even up to a year. In our case, we were limited to 3, 7, and 28 days. The findings from the hydraulic press were recorded from the following experiments in their respective tables. The blocks have been labeled block – (A through E) as differing amounts of SGA have been added for each block in the below experiments [10].

Experiment -1: Block – B (0.80% sodium gluconate)

The concrete mix was made using 266 grams of cement, 734 grams of sand, 2.14 grams of produced sodium gluconate admixture (SGA), and 115mL of water.

Table I: 3, 7, 28-day compressive strength for concrete mixture with 0.80% sodium gluconate.

Time/days	**Maximum Load/psi**
3	0
7	1300.0
28	2275.0

Experiment -2 Block – D (0.226% sodium gluconate)

The concrete mix was made using 266 grams of cement, 734 grams of sand, 0.3 grams of produced sodium gluconate admixture (SGA), and 115mL of water.

Table II: 3, 7-day compressive strength for concrete mixture with 0.226% sodium gluconate.

Time/days	**Maximum Load /KN**
3	1275.0
7	2320.0

Experiment -3 Block – C (0.113% sodium gluconate)

The concrete mix was made using 266 grams of cement, 734 grams of sand, 0.3 grams of produced sodium gluconate admixture (SGA), and 115mL of water.

Table III: 3, 7 day compressive strength for concrete mixture with 0.113% sodium gluconate.

Time/days	**Maximum Load /KN**
3	1400.0
7	2450.0

Experiment-4 Block – A (0.158% sodium gluconate, 1% industrial admixture)

The concrete mix was made using 266 grams of cement, 734 grams of sand, and 2.66 mL of p-con mixture (an industrial local water reducer), 0.42 grams of produced sodium gluconate admixture (SGA), and 115mL of water. The ratio of the admixtures was: SGA: p-con mix = 13.63: 86.26 and the total admixture (SGA+ p-con mix) used was 1.158%.

Table-IV: 3, 7, 28-day compressive strength for concrete mixture with 0.158% sodium gluconate, 1% industrial admixture (p-con mix).

Time/days	**Maximum Load /KN**
3	2023.3
7	2697.7
28	3750.0

Experiment-5 Block –E (0% sodium gluconate/blank)

The concrete mix was made using 266 grams of cement, 734 grams of sand, and 115mL of water.

Table-V: 3, 7, 28-day compressive strength for concrete mixture no sodium gluconate**.**

Time/days	**Maximum Load /KN**
3	2500.0
7	3587.5
28	4800

Some experiments could only be done for 3 days and 7 days as there was not enough time to complete the data collection for the 28th day before the submission date. Thus, this data set could be called an incomplete data set but still, from the 3-day and 7-day data we can say that the observations made in the next section make sense.

2.4.3 Observations

1. At the highest percentage of SGA (Block – B, 0.80%), the early strength and strength development was observed to be lowest and did not develop sufficiently on the 28th day. Thus, decreasing amount of sodium gluconate was used in the following experiments.

2. Early strength and 7-day strength development increased once the amount of SGA was lowered noticeably to 0.226% (Block -D). The 7-day strength of Block D is greater than the 28-day strength of block B. Thus, we concluded that the SGA is responsible for lowering the strength at higher dosages.

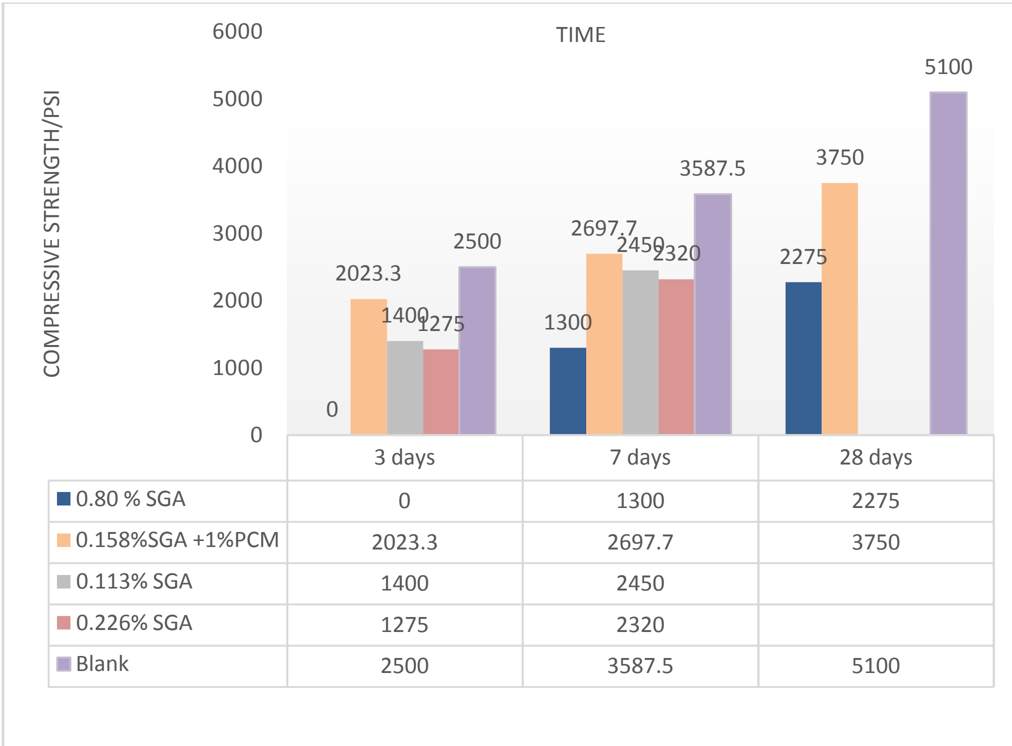

Fig.3. Bar chart for comparing compressive strength of different compositions of concrete blocks.

3. Lowering SGA further to 0.113% (Block C) increased the early compressive strengths even higher.

4. The hypothesis was thus made that adding other local industrial admixtures in controlled amounts might increase the strength of the admixture. So, an industrial admixture called p-con mix, a water reducer available in the lab, was added. It turned out that the hypothesis was correct.

5. After performing a few experiments, we found that when 0.158% sodium gluconate was taken with 1% p-con mix to create a concrete (Block-A) mixture, the early compressive strength and development of strength dramatically increased.

6. So, it was concluded that a strengthening admixture was required for this admixture to be used commercially, as the SGA admixture lowers the compressive strength of the blank concrete (Block E).

7. The blank (Block E) has had the highest compressive strength.

2.4.4. Characterization:

Infrared Spectrum of Sodium Gluconate

The peak around 3250 cm^{-1} is found due to the presence of the -OH stretching functional group in the compound. It is a robust and broad peak. We can observe C-H alkyl stretches near 2900cm^{-1}. An asymmetric C-O bond and a half stretching bands were observed around 1443 cm^{-1} for C-O bond and

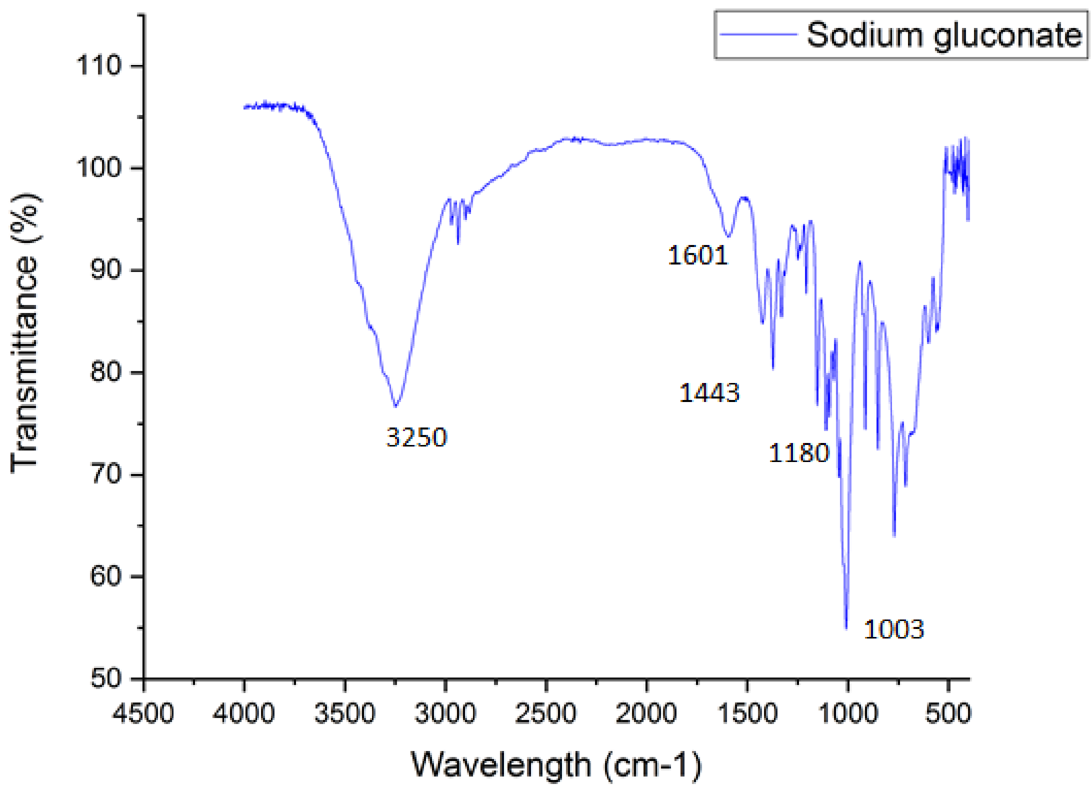

Fig.4. FT-IR spectrum of the prepared sodium gluconate crystals

A half stretching band is observed around 1390 cm^{-1}. At 1601cm^{-1} a weak peak is observed, which can account for the C=O group. But a clear peak isn't observed as it is not entirely a ketone or a carboxylic acid other than carboxylate form. Deformation vibrations in the plane, δ(OH), appear as a complex band in the range of wave number from 1390 cm^{-1} to 1450 cm^{-1}. The band of valence vibration, v(C-O), of the primary alcohol group, appears at 1038 cm^{-1} though it cannot be spotted distinctly. The band of valence vibration, v(C-O), of the primary alcohol group, appears at 1038 cm^{-1}

Bands at 1601 cm^{-1} in the spectrum of sodium gluconate are the results of asymmetric valency $_{asym}$(C=O) and symmetric vibrations v_{sym}(C=O) of a carbonyl group of carboxylate anion, which is highly deviated from the position it would be found at if it was solely a carbonyl compound. The peaks have been studied following [11].

Nuclear Magnetic Resonance Spectrum of Sodium Gluconate

The NMR analysis of sodium gluconate was relatively complicated and did not completely match with the literature. The approximate peak values are given below in the table.

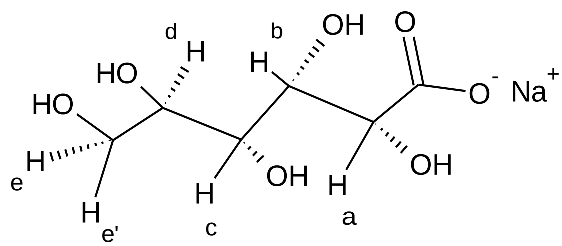

Fig.5. Formula of sodium gluconate with hydrogen atoms attached to carbon atoms labeled.

Table VI: Integral, chemical shift, multiplicity of the peaks in the NMR spectrum of sodium gluconate

Approximate Chemical Shift/ppm	Integral	Multiplicity	Hydrogen no.
5.055	1	doublet	a
4.473	2	doublet	e
3.690	4	triplet	c
3.557	3	multiplet	null and/or d
3.270	6	multiplet	e’ and/or d
3.072	3	triplet	b

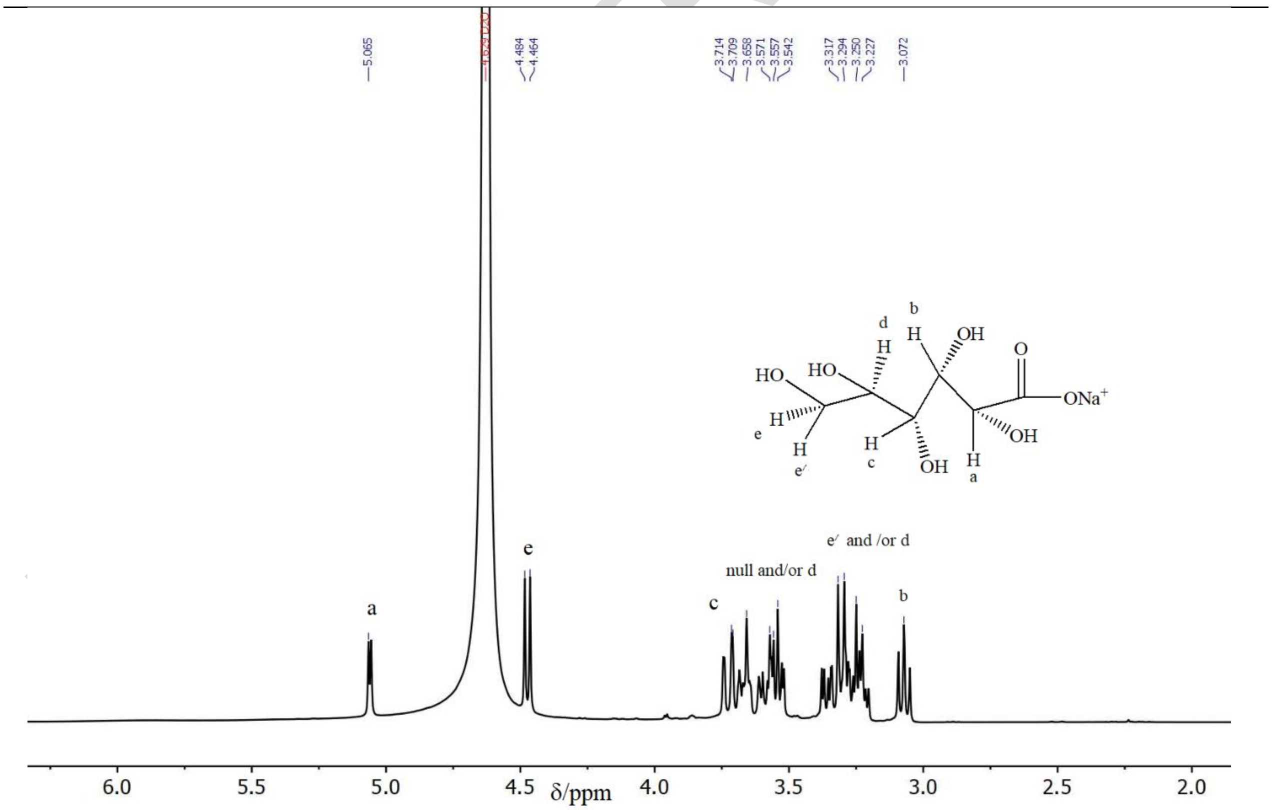

Fig.6.[1]H NMR spectrum of sodium gluconate in its anomeric forms

Based on the multiplicity and the chemical shift, we determined the above peaks to be the case. The doublet for H_a is the furthest downfield as it is attached to the oxygen that withdraws electron density directing from the neighboring atoms showing a peak at 5.055 $\delta$with only one adjacent H group. For glucose, a similar doublet at 5.2, is consistent with the existence of a proton bonded to a carbon bonded to two oxygens (the anomeric carbon, C1). We observe that the peaks of alpha-beta glucopyranose can be matched with the spectrum. Still, all peak values are shifted further towards up field region, representing a hybrid between the NMR of sodium gluconate and glucose.

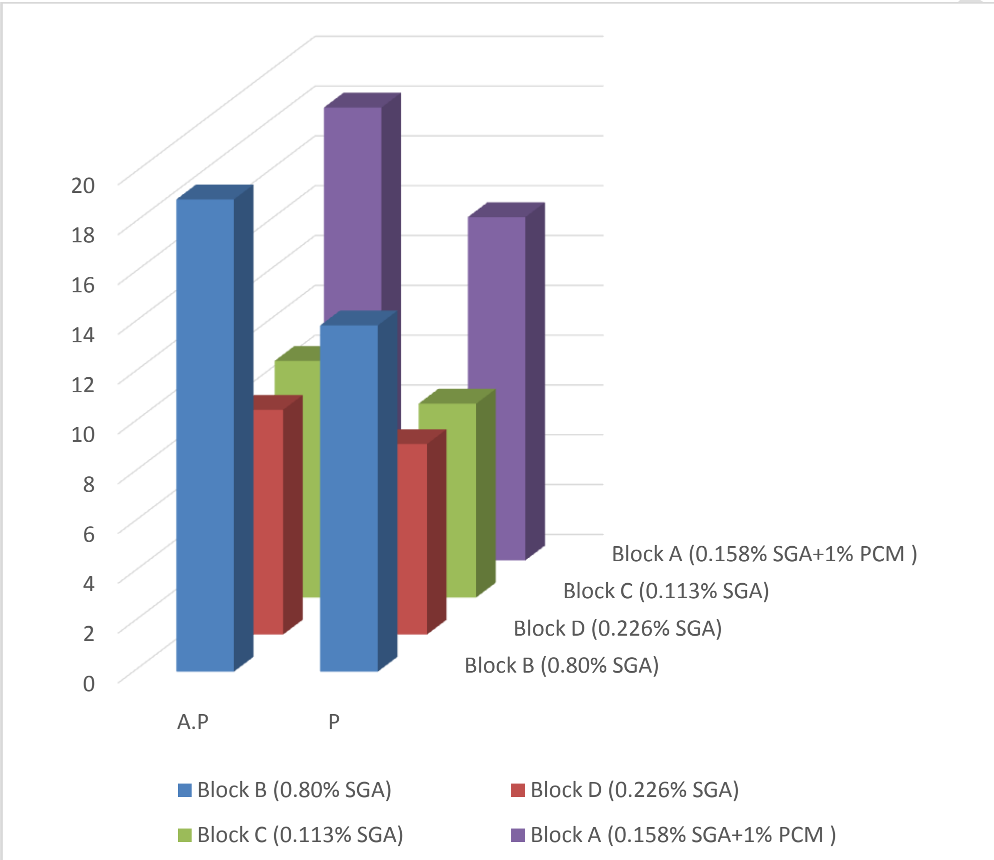

Fig.7. Bar chart comparing porosity and apparent porosity of different compositions of concrete blocks

3. RESULTS AND DISCUSSION

Chemical admixtures have been widely used to alter cement properties since the Roman era. But in the past 100 years, experimentation on concrete gave us the knowledge to theorize what sort of compound might affect the properties of cement in specific ways. Retarders have been an area of research for a long. This field gained interest in temperate regions like our country, where it is very much required for the cement not to set so fast that we cannot use it in the field or transport it properly, along with other reasons. That is why retarders were the primary subject of the study. Sodium gluconate and calcium gluconates are retarding admixtures that delay the setting time of cement. After the literature review, these compounds were selected as the primary target of synthesis. Sodium gluconate was successfully synthesized and characterized with a yield of 58.79%. Yield from the calcium gluconate experiment was 40.76% but couldn't be confirmed from NMR spectra as it showed no peak. Re-crystallization was the primary purification method, but it was evident that the sodium gluconate sample contained impurities of glucose. Calcium gluconate was excluded from further experiments on OPC as the produced batches did not show any retardation effects either. Furthermore, experiments on Ordinary Portland Cement (OPC) were performed, and observations included the retarder affecting early age strength development of the cement. As the dosage was increased, sodium gluconate lowered the compressive strength of OPC 2 x 2-inch concrete blocks. The bulk density decreased and then increased again as the dosage was reduced. To neutralize the effect of the low early-age strength development by the admixture, we used a locally available water reducer admixture which significantly increased the strength of the concrete blocks. The 28-day compressive strength of the particular block of mixed composition was found to be 3750 psi. The dosage of sodium gluconate was 0.158% (weight percent of cement), and that of locally available water reducer, p-con mix was 1% (Weight percent of cement). To achieve the necessary retardation, future studies are planned to be conducted so that strength development and retardation both effects are observed. It is also noteworthy that the impure dose of sodium gluconate required higher concentrations to retard OPC than the pure-grade sodium gluconate in the market. So, a slight variation of concertation will not show high retardation effects on the cement. As a result, it is easier to mix and handle as an admixture in the fields.

Retarders are solubility reducers as they reduce the solubility of the hydrating components in cement. Gypsum can retard the dissolution of the aluminate phase (C3A). Plaster of Paris can be used as a retarder. The primary function of retarders is to delay the concrete setting time, adversely affecting the subsequent strength development while permitting a subsequent reduction in the w/c ratio.[6]

Re-crystallization was used as the primary means of purification, but later it was understood. The sample of sodium gluconate most definitely contained impurities as we have observed multiplet in the NMR spectrum in the range of 3.2-3.8. The melting point differs significantly from the literature-reviewed value for sodium gluconate. The impurity is suspected to be glucose. Advanced purification methods, such as gas or liquid chromatography, are required to obtain purer yields of gluconate salt. The synthesized calcium gluconate showed no results in NMR or the cement setting time experiment; thus, it was removed from the cement study, and only sodium gluconate was focused upon. The sample of sodium gluconate synthesized was used to perform tests for the properties of Ordinary Portland Cement, such as normal consistency, setting time, compressive strength, bulk density, and durability.

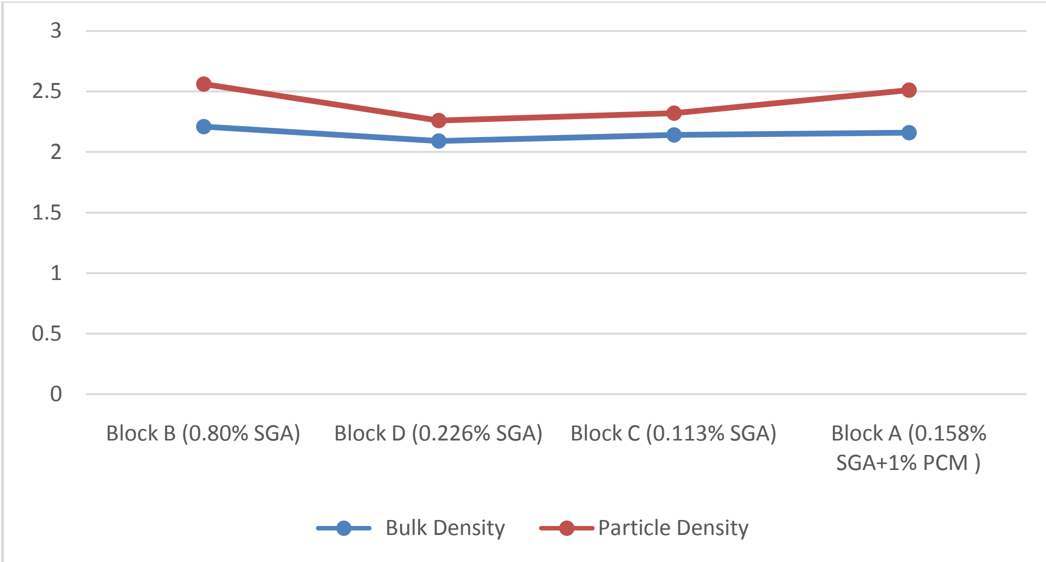

Fig.8. Line chart for comparing bulk density and particle density of different compositions of concrete blocks

All the tests for cement have been conducted according to the ASTM standards. It is evident from the results that the study is incomplete and that if impure sodium gluconate was to be synthesized in this manner and added to cement, then retardation of cement is found satisfying at 1% sodium gluconate by weight percent the Ordinary Portland Cement sample. And the compressive strength was found to be satisfactory at low concentrations of sodium gluconate, around 0.113%.

If the dosage of sodium gluconate is dropped, we can theorize that compressive strength will increase further, but that wouldn't serve our purpose of retardation. Further studies should be conducted to find an optimum mix of locally available admixture and the produced sodium gluconate to get the desired retardation effects with satisfactory compressive strength development. In all the tests done above, the best compressive strength result was observed at a sodium gluconate percentage of 0.158% and 1% of the p-con mix, a locally available water-reducing admixture (Block-A).

The compressive strength of Block A was 3750 psi on the 28th day. 1% sodium gluconate used in the setting time experiment resulted in an initial setting time of 75 minutes and a final setting time of 360 minutes. Future studies might involve using locally available admixture to hit that 1% admixture mark for sodium gluconate to get good retardation of setting time along with no compromise in the strength, which we have seen to increase with the use of appropriate strengthening agents. Block - A is also more durable in the experiments as its water absorption is lower. The higher bulk density of this block suggests the reason for the development in strength and also proves that the particular water reducer (p-con mix), in fact increases the strength of the concrete mix in question. General trends have been discussed for all mentioned properties with varying admixture content. This is a preliminary study due to the limited amount of time spent on the research and a lot of experimental struggles; thus, in the future, the idea is to expand the knowledge gained from these experimentations and find more concrete findings for such significant concrete admixtures.

4. CONCLUSION

In conclusion, sodium gluconate has been successfully synthesized and characterized using FTIR and ^{1}H-NMR spectroscopic techniques. The obtained sodium gluconate showed a yield of 58.79%. The yield for calcium gluconate was 40.76%. Early age strength development was hindered by the sodium gluconate produced. The addition of sodium gluconate to OPC was found to significantly extending the setting time, which would help to provide enough workability time for cement and concrete mixtures. However, when the amount of sodium gluconate is increased to -%, a reduction in compressive strength occurs due to the presence of excess gluconate ions in the cement matrix. These findings could provide valuable insights for the development of retarding admixtures for cement-based materials.

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