Electronic supplementary information (ESI)†

Sono-mechanical activation-assisted proton-catalyzed self-polymerization of AMPS in water: Hydrogel formation and its application as a functional additive in ordinary Portland cement†

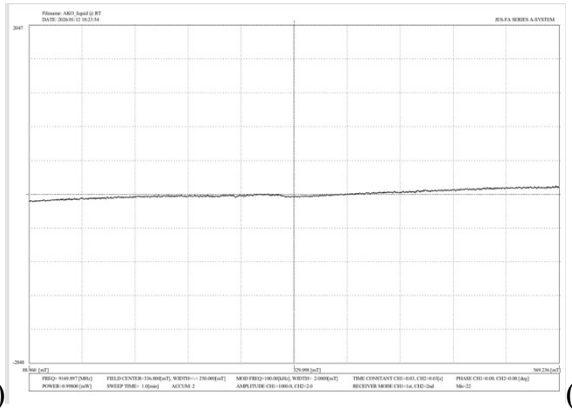
Kuldeep Rajpurohit, Sabrina A. Shaikh, Ashok K. Pandey* and Hemlata K. Bagla

Department of Nuclear and Radiochemistry, Kishinchand Chellaram College, HSNC University, Mumbai-400020, India

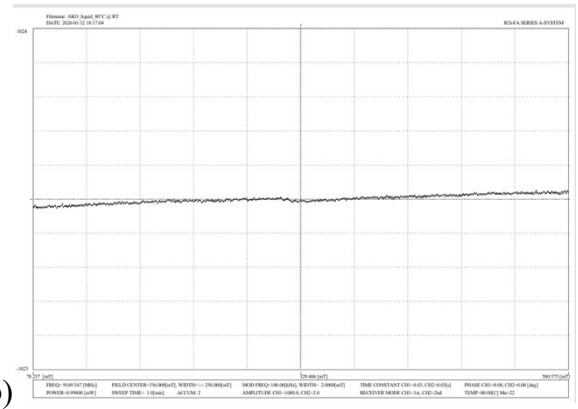
Email: ashok.pandey@kccollege.edu.in

Fig. S1. ESR spectra of AMPS in water at room temperature (a), 80 ºC (b), 120 ºC (c), 150 ºC (d), and 200 ºC (e).

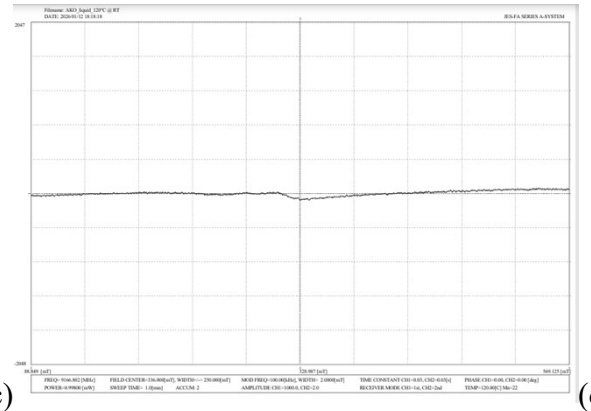
(a)



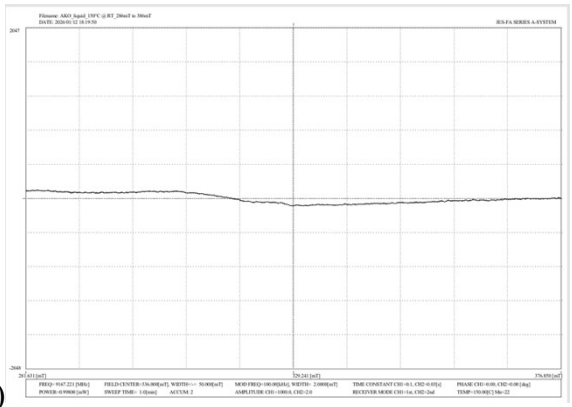
(b)



(c)



(d)



(e)

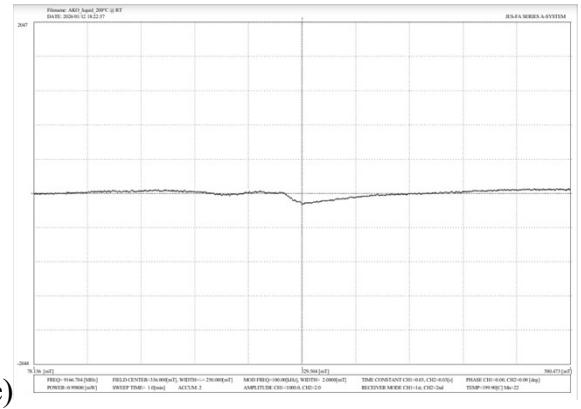


Fig. S2. FESEM images of Ca^{2+}-loaded crosslinked poly(AMPS) hydrogel.

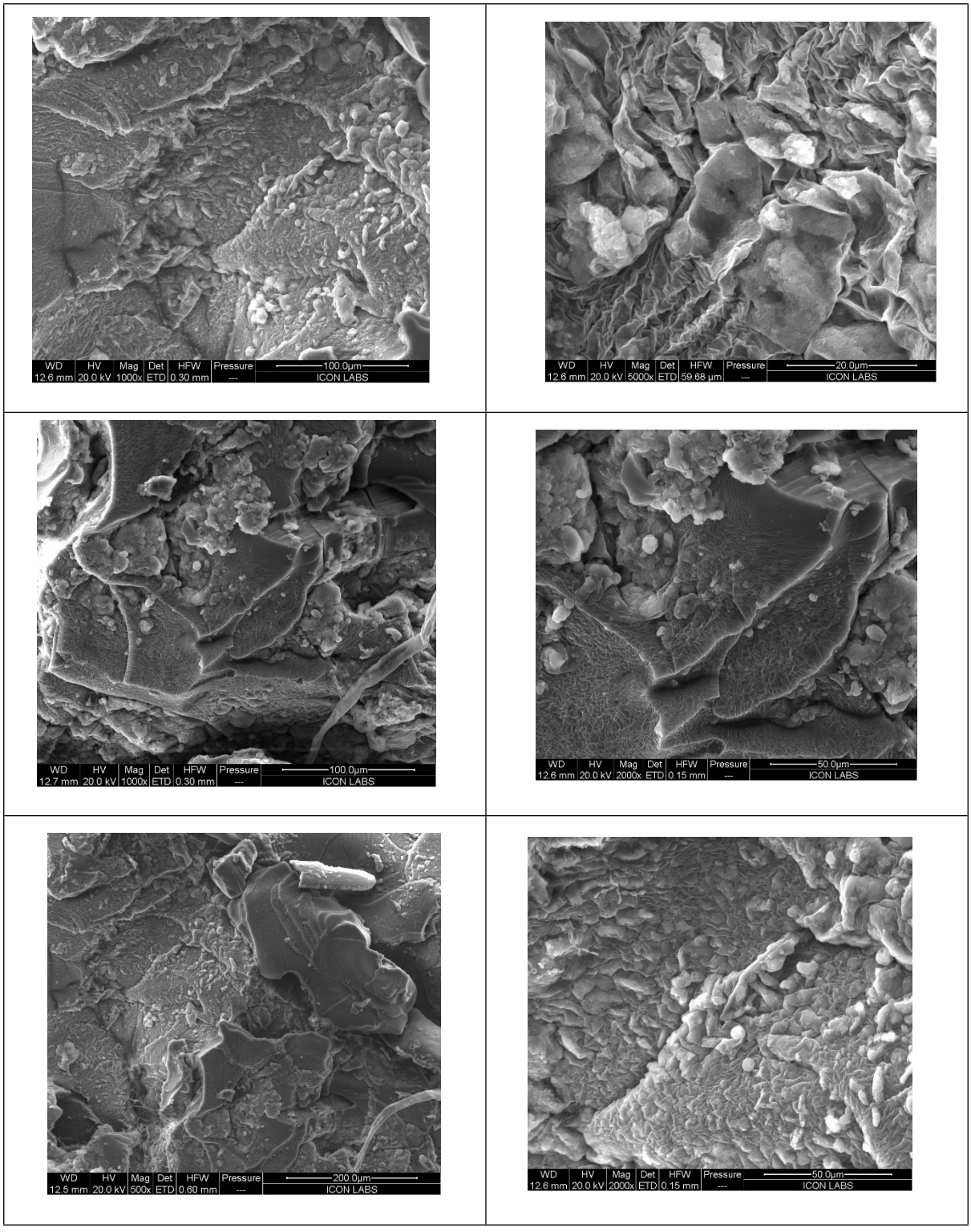


Fig. S3. EDS of crosslinked poly(AMPS) hydrogel.

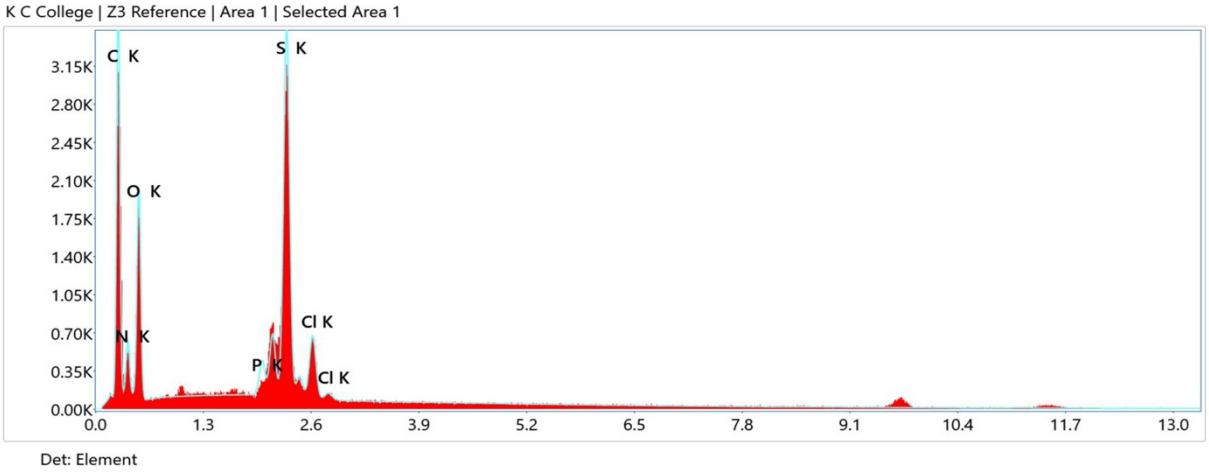
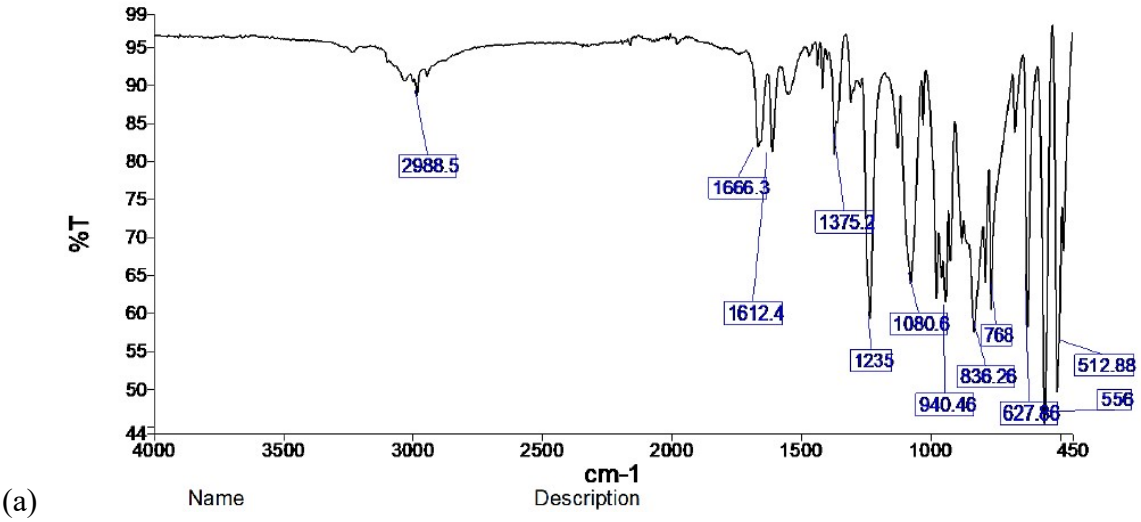
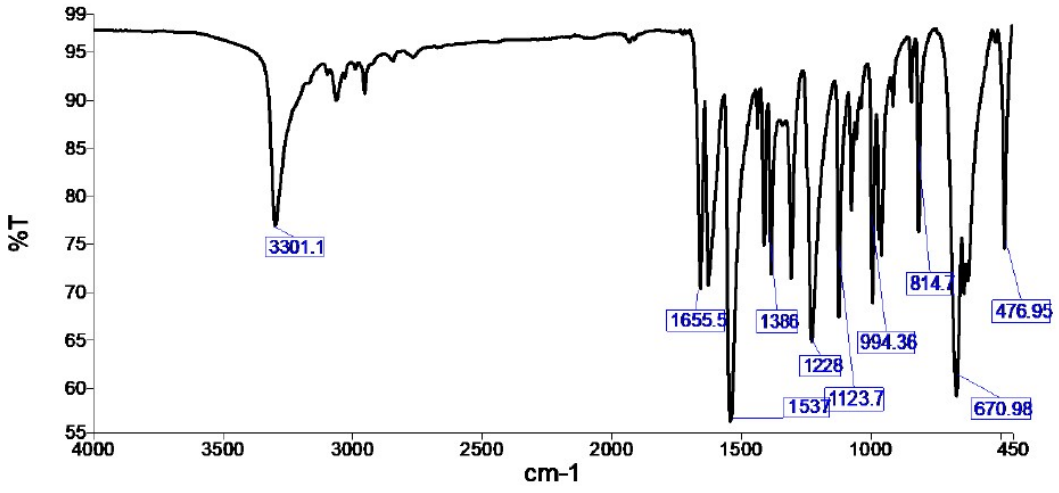


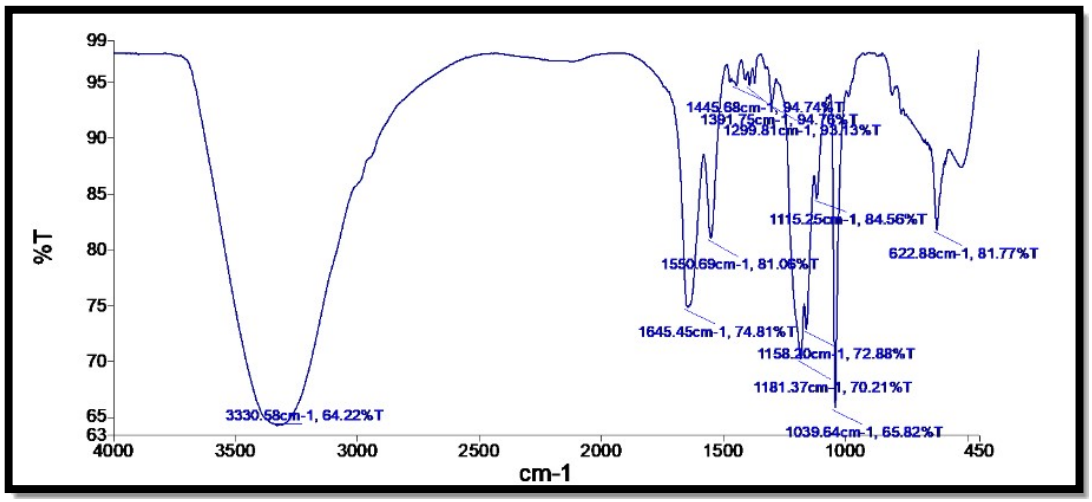
Fig.S4. FTIR Spectra of monomer AMPS (a), crosslinker MBA (b), and crosslinked poly(AMPS) hydrogel (c).



(a)

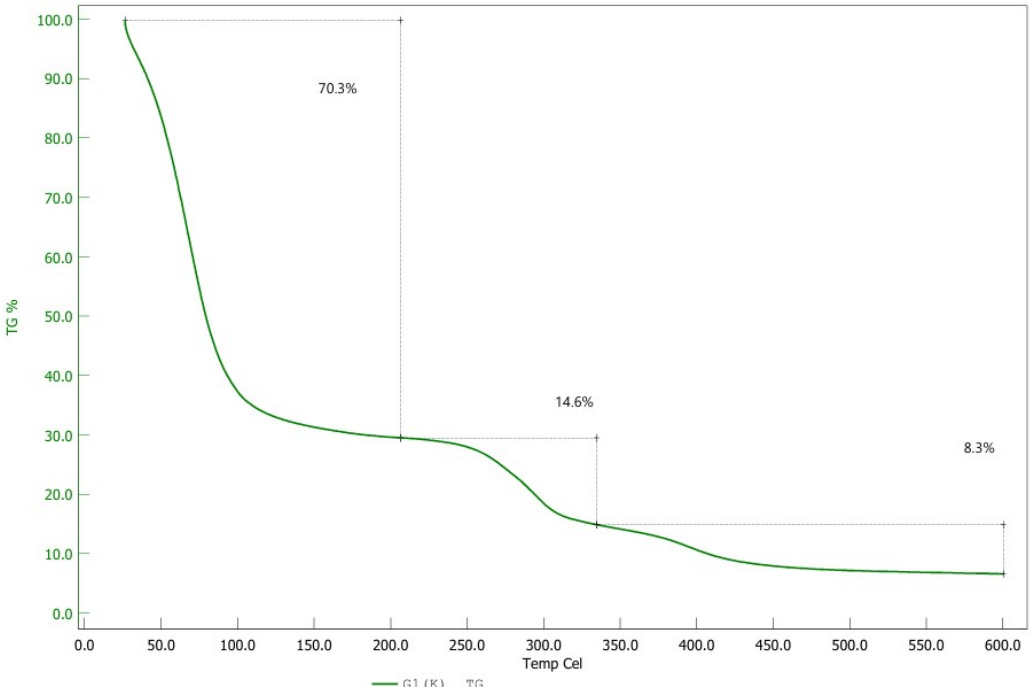


(b)

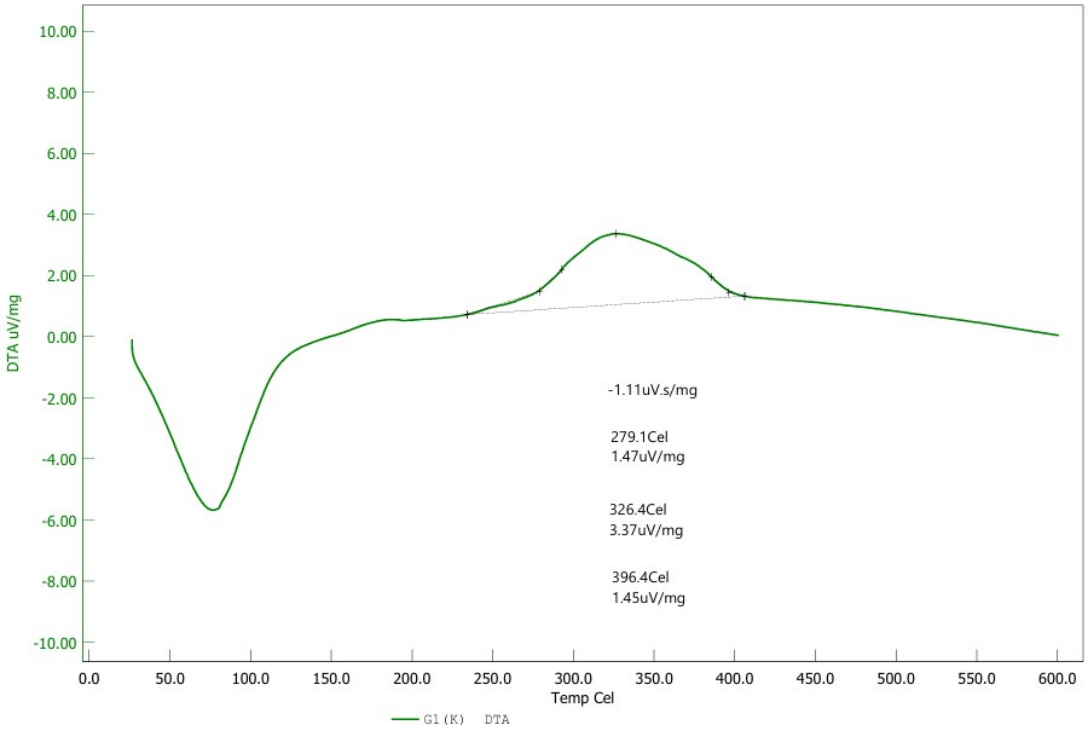


(c)

Fig. S5. The thermogravimetric analysis (TGA) (a) and differential thermal analysis (DTA) (b) of 5% MBA-crosslinked poly(AMPS) under nitrogen atmosphere.



(a)



(b)

Table S1. Formation of hydrogel using 2.4 mol/L monomer (10 mL) with 10 mol% MBA under ultrasound irradiation (20 kHz, 148 W/cm²).

Monomer	Additive	Additive conc.	Ultrasonication time (min)	Gel formation
AMPS	None	-	5	Formed
Acrylamide	None	-	30	Not formed
Methacrylic acid	None	-	30	Not formed
Acrylamide	AMPS	1:1 mol proportion	2.5	Formed
Acrylamide	H_2SO_4	0.1 M	4	Formed
Acrylamide	H_2SO_4	0.01 M	7	Formed
Acrylamide	H_2SO_4	0.001M	15	Not formed
Acrylamide	Methane sulfonic acid	1:1 mol proportion	4	Formed
Acrylamide	Tetra propyl ammonium chloride	1:1 mol proportion	10	Not formed

Supplementary Experimental Section

Hydrogel synthesis by ultrasonic probe sonicator

Hydrogel synthesis was done by dissolving AMPS and with different mol. % crosslinker MBA, then sonicated till gel was prepared (300± 10 sec.). Sono radiation generates reactive hydrogen radical (• H), which induces free radical polymerisation from the monomer. Then chain propagation and crosslinking through MBA result in the formation of three-dimension hydrogel.

Gel_1: Monomer AMPS with crosslinker MBA (5 mol. %), Gel_2: Monomer AMPS with crosslinker MBA (10 mol. %), Gel_3: Monomer AMPS with crosslinker MBA (15 mol. %) and gel 1, gel 2, gel 3 equilibrated with $CaCl_2$.

Setting time analysis

The setting time was assessed for thirteen mixtures: one without gel control, other twelve with different percentages of different gel. The mixtures were as follows:

1. Control: Cement (400 g) + Distilled Water (102 g)
2. With Gel_1 (0.3%): Cement (398.8 g) + G_1 (1.2 g) + Distilled Water (102 g)
3. With Gel_1 (0.5%): Cement (398.0 g) + G_1 (2.0 g) + Distilled Water (102 g)
4. With Gel_1 (1.0%): Cement (396.0 g) + G_1 (4.0 g) + Distilled Water (102 g)
5. With Gel_1 (2.0%): Cement (392.0 g) + G_1 (8.0 g) + Distilled Water (102 g)
6. With Gel_2 (0.3%): Cement (398.8 g) + G_2 (1.2 g) + Distilled Water (102 g)
7. With Gel_2 (0.5%): Cement (398.0 g) + G_2 (2.0 g) + Distilled Water (102 g)
8. With Gel_2 (1.0%): Cement (396.0 g) + G_2 (4.0 g) + Distilled Water (102 g)
9. With Gel_2 (2.0%): Cement (392.0 g) + G_2 (8.0 g) + Distilled Water (102 g)
10. With Gel_3 (0.3%): Cement (398.8 g) + G_3 (1.2 g) + Distilled Water (102 g)
11. With Gel_3 (0.5%): Cement (398.0 g) + G_3 (2.0 g) + Distilled Water (102 g)
12. With Gel_3 (1.0%): Cement (396.0 g) + G_3 (4.0 g) + Distilled Water (102 g)
13. With Gel_3 (2.0%): Cement (392.0 g) + G_3 (8.0 g) + Distilled Water (102 g)

The water requirement was set at 0.85 times the normal consistency (30%) of the cement weight. Sample preparation was carried out under laboratory conditions of temperature 27 ± 2 °C and relative humidity of 65 ± 5 % by gauging the cement with distilled water & cement with gel and distilled water within 3-5 minutes as per BIS code IS: 4031 (Part 4)-1988. Then filled the Vicat mould with cement paste and cement gel paste immediately placed mould in humidity chamber. For initial setting time (IST) mould placed under Vicat apparatus bearing needle then lowered till touch the surface of cement pastes and quickly released to penetrate into the block tested till it failed to pierce beyond 5.0 ± 0.5 mm from bottom of the mould and time calculated from when water was added to cement. For final setting time (FST) needle was replaced with an annular attachment and tested on cement paste till the needle made impression but attachment failed to do so and FST calculated from when water was added as per BIS standard IS: 4031 (Part 5)–1988.

Compressive strength testing

The compressive strength was assessed for different mixtures: one without gel control, with different percentages of different gel. The mixtures were as follows:

1. Control: Cement (200 g) + Sand (600 g) + Distilled Water (84 g)
2. With Gel_1 (0.3%): Cement (199.4 g) + Sand (600 g) + G_1(0.6 g) + Distilled Water (84 g)
3. With Gel_1 (0.5%): Cement (199.0 g) + Sand (600 g) + G_1(1.0 g) + Distilled Water (84 g)
4. With Gel_1 (1.0%): Cement (198.0 g) + Sand (600 g) + G_1(2.0 g) + Distilled Water (84 g)
5. With Gel_1 (2.0%): Cement (196.0 g) + Sand (600 g) + G_1(4.0 g) + Distilled Water (84 g)
6. With Gel_2 (0.3%): Cement (199.4 g) + Sand (600 g) + G_2(0.6 g) + Distilled Water (84 g)
7. With Gel_2 (0.5%): Cement (199.0 g) + Sand (600 g) + G_2(1.0 g) + Distilled Water (84 g)
8. With Gel_2 (1.0%): Cement (198.0 g) + Sand (600 g) + G_2(2.0 g) + Distilled Water (84 g)
9. With Gel_2 (2.0%): Cement (196.0 g) + Sand (600 g) + G_2(4.0 g) + Distilled Water (84 g)
10. With Gel_3 (0.3%): Cement (199.4 g) + Sand (600 g) + G_3(0.6 g) + Distilled Water (84 g)
11. With Gel_3 (0.5%): Cement (199.0 g) + Sand (600 g) + G_3(1.0 g) + Distilled Water (84 g)
12. With Gel_3 (1.0%): Cement (198.0 g) + Sand (600 g) + G_3(2.0 g) + Distilled Water (84 g)
13. With Gel_3 (2.0%): Cement (196.0 g) + Sand (600 g) + G_3(4.0 g) + Distilled Water (84 g)

Water content was calculated using the formula:

$$\text{Water (g)} = \left(\frac{Normal\ Consistency\ (\%)}{4} + 3\right)\% \ X\ (Cement + Sand)$$

The mortar Samples were prepared by gauging cement, sand, gel and distilled water in 3-5 minutes. The mortar was placed in a 70.66 mm cube mould in three layers, regularly tamped with a tamping rod, then compacted by vibrating on a vibration machine for 2 min. and at a specified speed of 12 000 ± 400 vib. /min. to remove entrapped air. Then moulds were stored in a humidity chamber of temperature 27 ± 2 °C and relative humidity ≥ 90% for 24 hr. Then demoulded the samples and transferred to the curing tank for 7, 28 and 60 days and tested for compressive strength with all in three replicates as per BIS standard IS: 4031 (Part 6)–1988.

Tensile strength testing

The tensile strength was measured for different mixtures: one without gel control, with different percentages of different gel. The mixtures were as follows:

1. Control: Cement (40 g) + Sand (120 g) + Distilled Water (16.8 g)
2. With Gel_1 (0.3%): Cement (39.88 g) + Sand (120 g) + G_1(0.12 g) + Distilled Water (16.8 g)
3. With Gel_1 (0.5%): Cement (39.80 g) + Sand (120 g) + G_1(0.20 g) + Distilled Water (16.8 g)

4. With Gel_1 (1.0%): Cement (39.60 g) + Sand (120 g) + G_1(0.40 g) + Distilled Water (16.8 g)
5. With Gel_1 (2.0%): Cement (39.20 g) + Sand (120 g) + G_1(0.80 g) + Distilled Water (16.8 g)
6. With Gel_2 (0.3%): Cement (39.88 g) + Sand (120 g) + G_2(0.12 g) + Distilled Water (16.8 g)
7. With Gel_2 (0.5%): Cement (39.80 g) + Sand (120 g) + G_2(0.20 g) + Distilled Water (16.8 g)
8. With Gel_2 (1.0%): Cement (39.60 g) + Sand (120 g) + G_2(0.40 g) + Distilled Water (16.8 g)
9. With Gel_2 (2.0%): Cement (39.20 g) + Sand (120 g) + G_2(0.80 g) + Distilled Water (16.8 g)
10. With Gel_3 (0.3%): Cement (39.88 g) + Sand (120 g) + G_3(0.12 g) + Distilled Water (16.8 g)
11. With Gel_3 (0.5%): Cement (39.80 g) + Sand (120 g) + G_3(0.20 g) + Distilled Water (16.8 g)
12. With Gel_3 (1.0%): Cement (39.60 g) + Sand (120 g) + G_3(0.40 g) + Distilled Water (16.8 g)
13. With Gel_3 (2.0%): Cement (39.20 g) + Sand (120 g) + G_3(0.80 g) + Distilled Water (16.8 g)

Water content was calculated using the formula:

$$\text{Water (g)} = \left(\frac{Normal\ Consistency\ (\%)}{4} + 3\right)\% \ X\ (Cement + Sand)$$

The mortar Samples were prepared by gauging cement, sand with and with gel and distilled water in 3-5 minutes. The mortar was placed in briquette mould in three layers with regular tamped with tamping rod then compacted by vibrating on vibration machine for 2 min. and specified speed of 12 000 ± 400 vib. /min. to remove entrapped air. Then moulds were stored in humidity chamber of temperature 27 ± 2 °C and relative humidity ≥ 90% for 24 hr. Then demoulded the samples and transferred to curing tank for 7, 28 and 60 days and tested for tensile strength with all in three replicates as per BIS standard IS: 4031 (Part 8)–1988.

Heat of hydration

The sample was prepared for heat of hydration with and without hydrogel in different composition as follow:

1. Control: Cement (60 g) + Distilled water (24 g)
2. With Gel_1 (0.3%): Cement (59.82 g) + G_1(0.18 g) + Distilled water (24 g)
3. With Gel_1 (0.5%): Cement (59.70 g) + G_1(0.30 g) + Distilled water (24 g)
4. With Gel_1 (1.0%): Cement (59.40 g) + G_1(0.60 g) + Distilled water (24 g)
5. With Gel_1 (2.0%): Cement (58.80 g) + G_1(1.20 g) + Distilled water (24 g)
6. With Gel_2 (0.3%): Cement (59.82 g) + G_2(0.18 g) + Distilled water (24 g)
7. With Gel_2 (0.5%): Cement (59.70 g) + G_2(0.30 g) + Distilled water (24 g)
8. With Gel_2 (1.0%): Cement (59.40 g) + G_2(0.60 g) + Distilled water (24 g)
9. With Gel_2 (2.0%): Cement (58.80 g) + G_2(1.20 g) + Distilled water (24 g)
10. With Gel_3 (0.3%): Cement (59.82 g) + G_3(0.18 g) + Distilled water (24 g)

11. With Gel_3 (0.5%): Cement (59.70 g) + G_3(0.30 g) + Distilled water (24 g)
12. With Gel_3 (1.0%): Cement (59.40 g) + G_3(0.60 g) + Distilled water (24 g)
13. With Gel_3 (2.0%): Cement (58.80 g) + G_3(1.20 g) + Distilled water (24 g)

The sample was mixed by hand for 4 minutes, then poured into a plastic cork and sealed with wax. It was placed in a vertical position and tested after 7, 28, and 60 days in three replicates.

Determination of the heat capacity of the calorimeter poured 288±0.1 ml 2N HNO_3 and 9.6±0.1 ml HF solution into the calorimeter and stirred to allow the uniform temperature, introduced ZnO (7 g, ignited at 900-950 °C and cooled over 2.5 hr.) and measured the final heating correction of the solution.

$$\text{Heat Capacity (J/°C)} = \frac{Mass\ of\ ZnO(1084\ -\ 0.9\varphi\ +\ 0.5\varphi_0)}{Corrected\ temp\ rise}$$

Determination of Heat of Solution of Anhydrous Cement introduced anhydrous cement (3g) in a solution of 288±0.1 ml 2N HNO_3 and 9.6±0.1 ml HF and measured the rise in temperature.

$$\text{Heat of Solution of Anhydrous Cement (kJ/kg)} = \frac{Heat\ capacity\ x\ corrected\ temperature - rise}{Mass\ of\ sample\ corrected\ for\ ignition\ loss} - 0.8(\varphi_0 - \varphi)$$

Determination of Heat of Solution of Hydrated Cement ground the cement paste formed in plastic cork and passed through 850µm sieve rapidly and introduced in 288±0.1 ml 2N HNO_3 and 9.6±0.1 ml HF solution and measured the temperature rise.

$$\text{Heat of Solution of Hydrated Cement (kJ/kg)} = \frac{Heat\ capacity\ x\ corrected\ temperature - rise}{Mass\ of\ sample\ corrected\ for\ ignition\ loss} - 1.7(\varphi_0 - \varphi)$$

where: φ_0- Room temperature, φ- final temperature of thermometer in °C

Heat of hydration (kJ/kg) = Heat of Solution of Anhydrous Cement – Heat of Solution of Hydrated Cement, as per IS: 4031 (Part 9)–1988.