Carbonation of Ulexite Ore Waste for CO2 Sequestration

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Abstract: -3 mm ulexite ore containing 20-25 % B_2O_3, being a concentration waste is accumulated in mine area. Boron content of this waste dissolves by rain and snow waters and passes to soil, surface water and underground water and can be caused to pollution. For this reason, boron content of this waste must be removed or gained.As a result of industrialization, also, the amount of carbon dioxide given to atmosphere increases, day by day, and causes to global heating and climate change. For this reason, it is required to be removed carbon dioxide in flue gases. In this study, sequestration of carbon dioxide with ulexite ore waste was investigated under high pressures and at temperatures of 90 to 170°C. In the experiments, temperature, carbon dioxide pressure, solid-to-liquid ratio, particle size and stirring speed were chosen as parameters. In result, sequestration rate increased with increase in temperature and carbon dioxide pressure, and with decrease in solid-to-liquid ratio and paticle size. Stirring speed did not affect the sequestration rate. Also, boron and carbon dioxide, which form the risk for environmental were converted to sodium pentaborate and calcium carbonate by this process, respectively.Also, kinetics of reaction between carbon dioxide and ulexite waste was examined according to experimental data and determined that reaction kinetics fitted to ash diffusion control, stated as $1-3(1-X)^{2/3}+2(1-X) = kt^m$ and activation energy was found as 20.5 kJ.mol^{-1}.

Keywords: Waste ulexite, carbon dioxide, global warming, climate change

Introduction

 CO_2 content of the atmosphere has increased significantly and rapidly in recent years reaching 3841 ppm in 2007, with an annual mean growth rate of almost 21 ppm since 2000. In order to prevent CO_2 concentrations in the atmosphere rising to unacceptable levels, carbon dioxide can be separated from the flue gases of power plants and subsequently sequestrated. Various technologies for carbon dioxide sequestration have been proposed[1].

An alternative sequestration method is mineral CO_2 sequestration method in which CO_2 is chemically stored in solid carbonates by the carbonation of minerals. Mineral CO_2 sequestration has some fundamental advantages compared to other sequestration routes. The formed products are thermodynamically stable and therefore the sequestration of CO_2 is permanent and safe. In order to be able to react with acid CO_2, the mineral has to provide alkalinity[2].

 The rates of carbonation reactions   at atmospheric conditions are much too slow for an industrial process. Therefore, research focuses on increasing the reaction rate in order to obtain an industrial viable process[6-9].

Carbonation of industrial alkaline residues can be used as a CO_2 sequestration technology to reduce carbon dioxide emissions. The production of valuable products by utilizing CO_2 has been the objective of many studies in recent years [10-13].

Rendek *et al.* [14] performed their accelerated carbonation experiments in a high pressure vessel at room temperature for municipal solid waste incinerator ash. The pressure improved the kinetics of the reaction but did not affect the final amount of carbonates formed[15].

Another type of industrial solid residues that could be used for CO_2 sequestration is air pollution control equipment residue, an alkaline residue that can be collected from various incinerator plant flue gas clean-up systems. In a study by Baciocchi *et al* it has been determined to correspond to a CO_2 storage potential of about 150 kt/yr (120 g of CO_2/kg of residue) of this residue [16]. However, it has been stated that this process has limited volume potential.
Baciocchi *et al.* [17] investigated the kinetics of gas-solid carbonation of APC residues when subjected to a flux of CO_2 (10 vol-%) in argon. In this study with two stages, the kinetic analysis was limited to the first stage of the carbonation process. But, it was not taken into account the second stage data associated with CO_2 diffusion through a product layer.

Back *et al.* [18] investigated the CO_2 uptake potential of lignite fly ashes. They resulted in a maximum CO_2 binding capacity of around 0.1 kg CO_2/kg ash in 1 h, corresponding to 0.5% of the CO_2 emissions from a brown coal firing plant in an experiment performed in 30 °C under atmospheric pressure (pCO_2 = 0.1) and a low S/L ratio (1/80).
By upgrading a waste product into a product of high commercial value, expensive CO_2 sequestration processes could become economically feasible. Katsuyama *et al.* [19] studied the feasibility of producing $CaCO_3$ from waste cement by first extracting calcium from pulverized waste cement in a water slurry at high CO_2 pressure (several MPa), followed by the precipitation of $CaCO_3$ from the extracted solution at lower CO_2 pressures. In result, they produced high purity $CaCO_3$ from waste cement at relatively high reaction rates.

In this study presented here, -3mm ulexite ore waste was used to capture CO2 in flue gas from power stations in aqueous solutions under high pressures and at high temperatures. In result, CO2 by ore waste and boron content of ore waste was recovered.

Experimental Procedure

Ulexite ore waste used in these studies has been supplied from Bigadiç Boron Establishments. After the ore waste was dried in air, it was ground by a laboratory grinder and fractionned by sieving with the standard sieves. This ore waste contained 23,6% B_2O_3, 9,21% SiO_2, 25,48% CaO, 6,67% MgO, 2,25% Na_2O, 0,51% Al_2O_3, 0,09% Fe_2O_3, 1,13% SrO, 31,21% heating loss as according to XRF analysis. CO_2 gas was supplied as tube from Habaş, Turkey.

All tests were carried out in a two-liter magnetic-stir-drive PARR autoclave. The CO_2 pressure applied was controlled by a pressure-measuring device (Fig. 1), and the temp. of the reaction in the reactor was provided by an automatically controlled heater underneath the stainless-steel vessel, which allowed the slurry to be taken out of the device for separation by filtration of the solid particles. A 50 kg CO_2 tank containing the gas at 200 bar pressure was used as the CO_2 source.

In the experiments, after 300 mL water was taken in the reactor, a predetermined amount of the ulexite waste was placed into the vessel. After reactor was adjusted to desired temperature and the stirrer to desired speed, CO_2 injection was performed up to desired pressure. The pressure was continuously monitored and more CO_2 was injected as the pressure decreased either due to leaks or chemical reaction. At the end of the desired test time the stirring stopped and the slurry was cooled by running water through cooling coils in the solution. When the temperature fell below 85 °C, the pressure was bled off and the

slurry was taken out of the device. The slurry was filtered, and the solids were dried at 105 ^{o}C, weighed, and sampled for analysis. Na, Ca and B_2O_3 analysis was performed in solution.

B_2O_3 fractions passing to the solution were calculated as follows:

$$B_2O_3 \text{ fraction passing to the solution} = \frac{amount\ of\ B_2O_3\ passing\ to\ the\ solution}{total\ amount\ of\ B_2O_3\ in\ original\ sample} \tag{1}$$

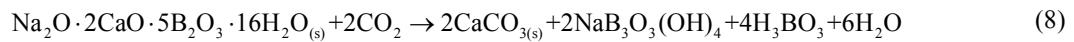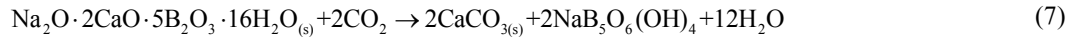| Parameters	Parameter values					
Temperature(K)	363	378	393	413*	433	443
Solid-to-liquid(g/mL)	0,15	0,20*	0,25	0,30		
Stirring speed(rpm)	300	500*	700			
CO_2 pressure(Bar)	5	10	15	20*		
Particle size(meş)	-80 +100	-60 +80	-45 +60*	-30+45		

*Parameters kept constant

Table 1. Parameters and their values

Results and Discussion

In view of its reactivity with carbon dioxide, ulexite ore waste has been proposed for the reduction of greenhouse gas emissions from utility power plants.
The reactions between ulexite and CO_2 in aqueous solution are given in Equations 7, 8 and 9.

$$Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 16H_2O_{(s)} + 2CO_2 \rightarrow 2CaCO_{3(s)} + 2NaB_5O_6(OH)_4 + 12H_2O \tag{7}$$

$$Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 16H_2O_{(s)} + 2CO_2 \rightarrow 2CaCO_{3(s)} + 2NaB_3O_3(OH)_4 + 4H_3BO_3 + 6H_2O \tag{8}$$

Also, the reaction between colemanite and CO_2 as follows;

$$2CaO \cdot 3B_2O_3 \cdot 5H_2O_{(s)} + 2CO_{2(g,aq)} + 4H_2O \rightarrow 2CaCO_{3(s)} + 6H_3BO_{3(s,aq)} \tag{9}$$

The ratios of the ionic borate species depending on the pH values are given in Figure 2. The pH value during the chemical reaction was recorded as between 6.5-7; at this pH value the borate species $B_5O_6(OH)_4^-$, $B_4O_5(OH)_4^-$, $B_3O_3(OH)_4^-$ and $B(OH)_3$ have been found in aqueous solution [20]. The amount of CO_2 captured in solution was proportional to the borate ion concentrations.

The parameters used in this study were particle size, solid-to-liquid ratio, CO_2 pressure, stirring speed and temperature. In examining the effect of particle size, solid-to-liquid ratio was kept constant as 0.2 g/mL, CO_2 pressure as 20 bar, stirring speed as 500 rpm and temperature as 323K. Particle size levels were -30 +45, -45 +60, -60 +80, -80 +100 mesh. Results are given graphically in Figure 1. According to these results, dissolution rate increased with decreasing particle size.
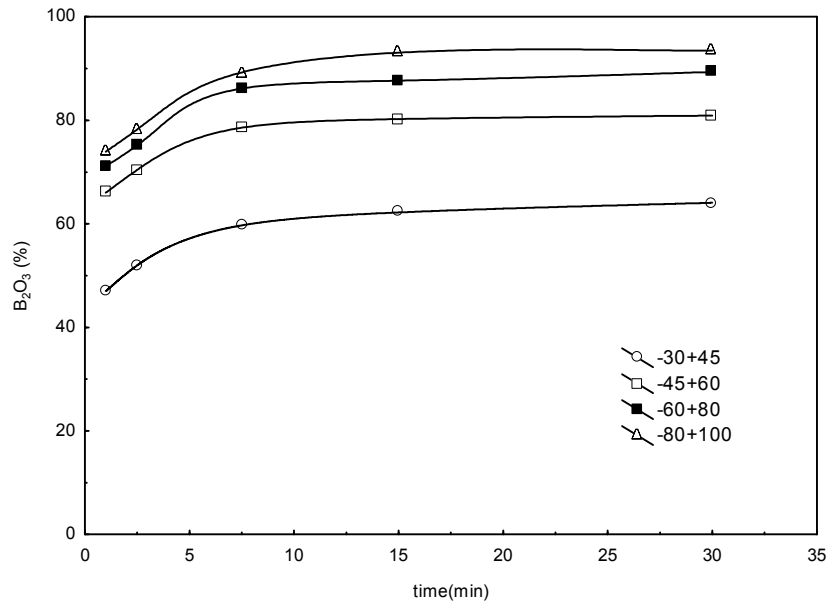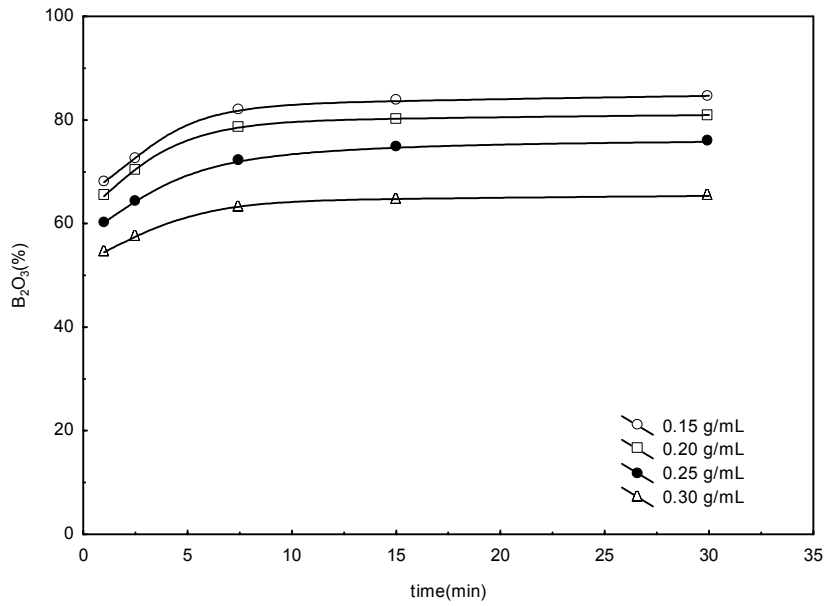
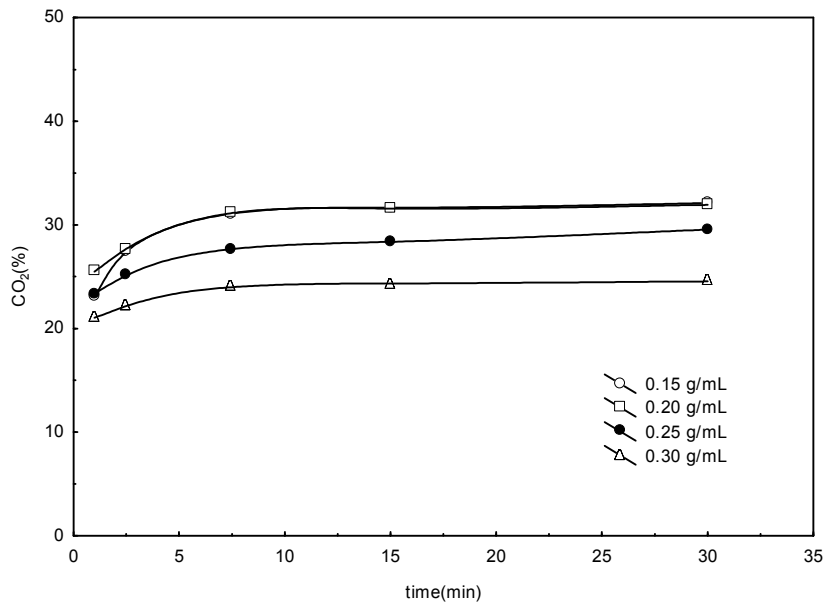**Figure 1**. The effect of particle size on dissolution of ulexite ore waste in CO_2 containing water
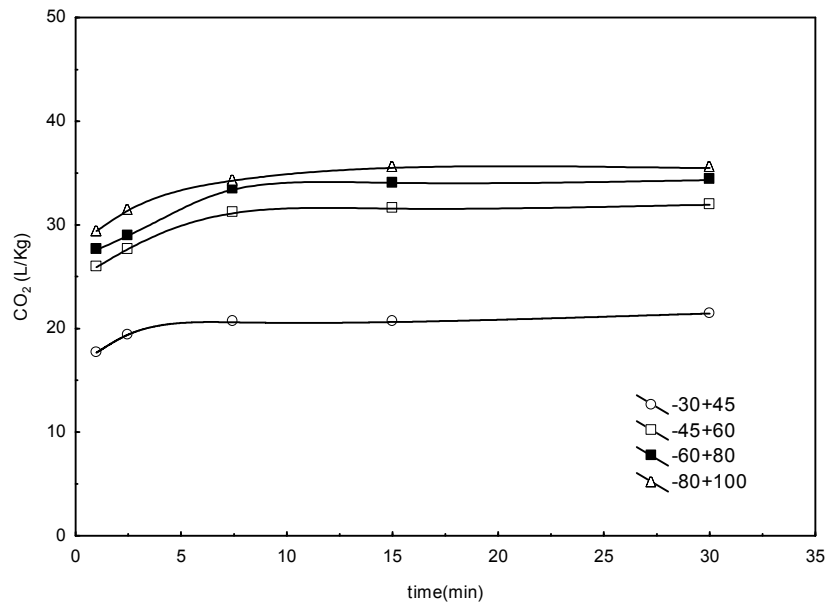
Figure 2. The effect of particle size on CO_2 sequestration by ulexite ore waste.

The effect of solid-to-liquid ratio was investigated for 0.15, 0.20, 0.25 and 0.30 g/mL values of solid-to-liquid ratio, so that particle size was kept constant in -45 +60, CO_2 pressure in 20 bar, stirring speed in 500 rpm and temperature in 413 K. The results are given graphically in Figure 3. According to the results, increasing the solid-to- liquid ratio causes to decrease of dissolution rate. It is given the effect of solid-to-liquid ratio on CO_2 sequestration by ulexite ore waste in Figure 4..
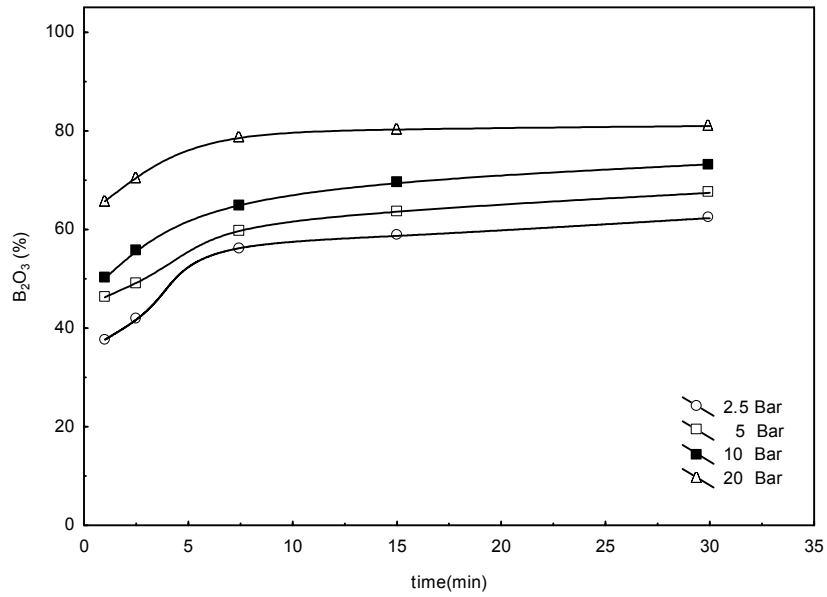
**Figure 3**. The effect of solid-to-liquid ratio on dissolution of ulexite ore waste in CO_2 containing water

Figure 4. The effect of solid-to-liquid ratio on CO_2 sequestration by ulexite ore waste.

The effect of CO_2 pressure on dissolution of ulexite ore waste was examined at the CO_2 pressures, 20, 15, 10 and 5 atm. Particle size was kept constant in -45 + 60 μm, solid-to-liquid ratio in 0.2 g/mL, stirring speed in 500 rpm and temperature at 413 K. The results are given graphically in Figure 6. According to the results, as CO_2 pressure increases, dissolution rate increases. It is given the effect of pressure on CO_2 sequestration by ulexite ore waste in Figure 6.

Figure 5. The effect of CO_2 pressure on dissolution of ulexite ore waste in CO_2 containing water
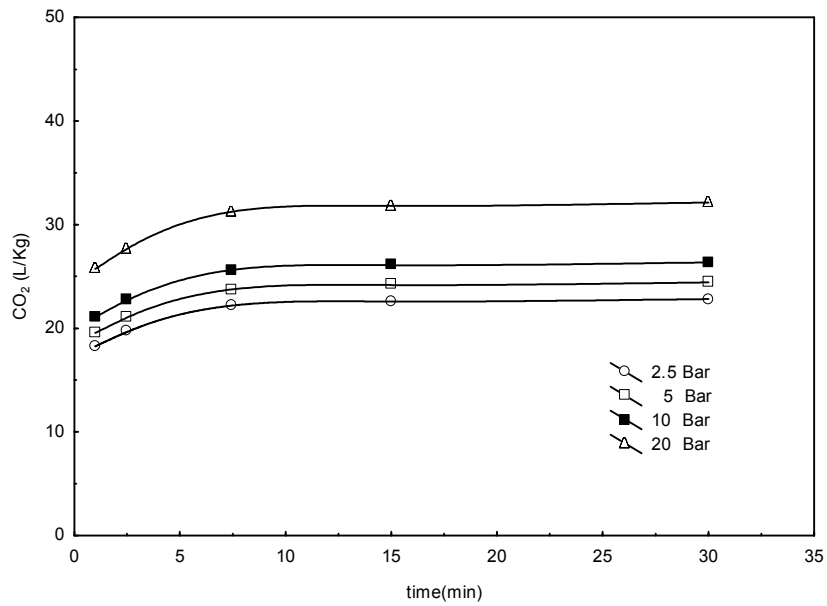
Figure 6. The effect of pressure on CO_2 sequestration by ulexite ore waste.

The solubility product of calcium carbonate at STP is 5×10^{-9}. First, the gas phase (CO_2) must dissolve in the solution:

$$CO_{2(g)} + H_2O \quad H_2CO_{3(aq)} \tag{10}$$

According to Henry's Law, the concentration of $H_2CO_{3(aq)}$ is proportional to the CO_2 partial pressure (P_{CO2}). At standard temperature and pressure (STP), Henry's constant (KH) = 29.4 atm/mol/L. H_2CO_3

concentration increases with increasing CO_2 pressure at 25°C. Using the high-pressure correction to Henry's law would only lower the calculated concentration by approximately a factor of 1.25[1].

H_2CO_3 dissociates according to the following:

$$H_2CO_{3(aq)} \quad H^+_{(aq)} + HCO^-_{3(aq)} \qquad K_{a1} = 4.5 \times 10^{-5} \tag{11}$$

HCO_3^- dissociates further as follows:

$$HCO^-_{3(aq)} \quad H^+_{(aq)} + CO^{2-}_{3(aq)} \qquad K_{a1} = 4.5 \times 10^{-11} \tag{12}$$

At equilibrium, when no other acid is in the solution, $[H^+]$ and $[HCO_3^-]$ are equal and

$$\left[CO_3^{2-} \right] = \frac{4.7 \cdot 10^{-11} \left[HCO_3^- \right]^2}{H^+} \tag{13}$$

These equations indicate that increased CO_2 pressure lowers pH, and this would help to leach calcium from the ulexite as it has been shown in some leaching tests of ulexite. Increasing CO_2 pressure also increases $[HCO_3^-]$ and, thus, CO_3^- which is required for the precipitation of calcium carbonate. However, because K_{a2} is small compared K_{a1}, simply raising the pressure of CO_2 only generates small amount of CO_3^{2-}. In that case, the concentration of carbonic ion is very small, and thus a very high calcium ion concentration is required to precipitate calcium carbonate. The precipitation of calcium carbonate will increase by the increase in carbonic-ion concentration with Na ions passed solution with ulexite dissolution.

The solubility of calcium carbonate decreases with increase in temperature. the dissolution reaction for carbonate minerals is exothermic, which results in higher temperatures favoring the solid phase over dissolved ions. The solubility of calcium carbonate in the presence of sodium carbonate is less than 0.5 p. p. m.

Dissolution data from experiments were evaluated bt a statistical program and the following model was found for dissolution. As result, dissolution process fit to ash diffusioncontrols kinetics. That stirring speed isn't effective on the dissolution and activation energy of 20.474 kj.mol^{-1} show that process rate is controlled by ash diffusion controls kinetics. Convenience of this model was controled by drawing a graph of dissolution values from this model versus experimental data(Figure 7). In result, it was determined that the model is suitable.

$$1-3(1-X)^{(2/3)} + 2(1-X) = 1091(P)^{0.43}(S/L)^{-0.84}(PS)^{-0.91} e^{-\frac{20.474}{RT}} t^{0.2} \tag{15}$$
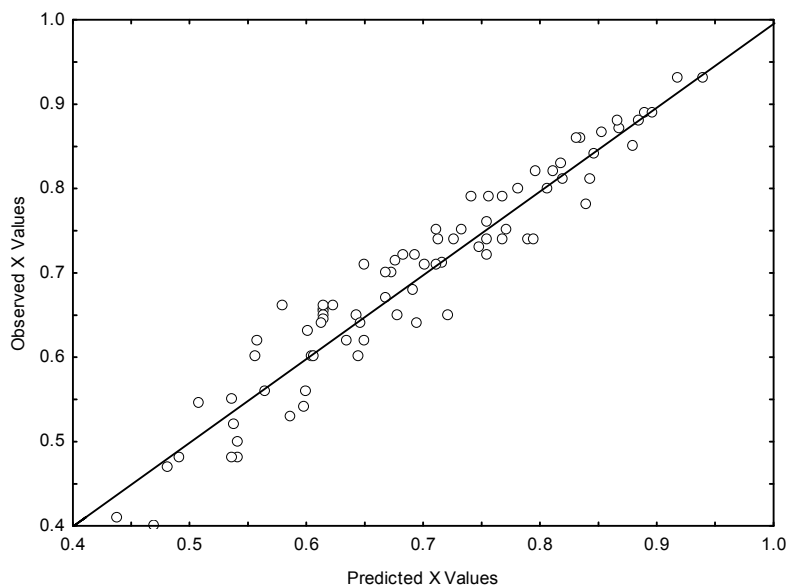
Figure 7. Graph of observed values versa predicted values from model

Acknowledgements

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