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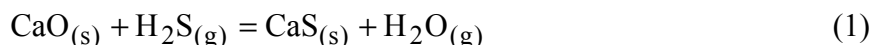
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A Reusable Calcium-Based Sorbent for Desulfurizing Hot Coal Gas

Key Words: calcium-based sorbent, coal gas, desulfurization, core-in-shell pellet

Introduction

There is a continuing need for an inexpensive, regenerable sorbent for desulfurizing hot coal gas. Such a material is needed especially for advanced power generating systems including integrated gasification combined-cycle (IGCC) systems and other systems which employ various topping cycles (Bakker et al. 1998). Maximum power generation efficiency can be achieved by cleaning the gas at nearly gasifier outlet temperatures which can range up to 1200 K or more. One of the few materials which is an effective absorbent at these temperatures is CaO because the following reaction is both thermodynamically and kinetically favorable (Westmoreland and Harrison 1976; Westmoreland et al. 1977):



Furthermore, since CaO can be derived from limestone or dolomite, which are plentiful and inexpensive, much consideration has been given to the use of calcium based sorbents (van der Ham et al. 1996, Abbasian 1998). Unfortunately, these materials tend to be soft and friable and do not withstand much handling or reuse. To overcome this problem Voss (1982) had previously proposed pelletizing pulverized limestone with a clay binder.

More recently an alternative method of pelletizing limestone or other calcium-bearing materials became the subject of an investigation at Iowa State University and promising results have been reported (Akiti et al. 2001, 2002; Wheelock and Akiti 2002). This method was demonstrated by first pelletizing powdered limestone or plaster of Paris and then applying a porous but strong protective shell to each pellet. Initially, the pellet shells were made of hydraulic cement, but then it was discovered that more durable shells could be made by coating the pellet cores with a mixture of limestone and alumina particles followed by calcination at 1373 K to partially sinter the shell material. The resulting shells were strong, porous, and resistant to large temperature changes. Since a core-in-shell sorbent holds great promise, the present project was undertaken.

Objective

The overall objective of this project has been to develop a superior, regenerable, calcium-based sorbent for desulfurizing hot coal gas. The sorbent should be strong, durable, inexpensive to manufacture, and capable of being reused many times. To achieve these objectives the project has focused on the development of the very promising core-in-shell sorbent.

Approach

A largely experimental approach has been used for achieving the project objective. The methods used for obtaining the present results are described below.

The pellet cores were made either of Iowa limestone or commercial-grade plaster of Paris. The limestone was obtained from a quarry operated by Martin Marietta Aggregates located near Ames, Iowa, and it had a CaCO_3 content in excess of 99%. The material was ground and screened to provide particles between 0.2 and 5.0 μm for pelletizing. Two commercial grades of plaster of Paris were utilized. The first material was impure with the following composition: 77% calcium sulfate hemihydrate, 15% calcite, 6% dolomite, and 2% other minerals. This material consisted of particles smaller than 37 μm . The second material utilized was much purer with a calcium sulfate hemihydrate content in excess of 99%. The material as received consisted of particles between 0.2 and 5.0 μm . Sorbent shells were made largely of two different grades of alumina supplied by Alcoa. The predominant grade was T-64 tabular alumina having a median particle diameter of 8.65 μm . The other grade was A-16 SG alumina powder having a median particle diameter of 0.88 μm .

The core-in-shell pellets were prepared in two stages with a bench-scale, revolving drum pelletizer which had a diameter of 25 cm and was operated between 60 and 80 rpm. The pellet cores were prepared first by placing a measured quantity of powder in the drum, and as the drum revolved the powder was sprayed intermittently with water or a dilute lignin solution. Water was used for plaster of Paris and the lignin solution for limestone. More material was added during pelletization to increase the size of the pellets. When the pellets reached a desired size, they were tumbled for an additional period of time to improve their sphericity and uniformity. The finished cores were separated by screening, and the cores which fell between 3.33 and 3.96 mm were collected for coating. Pellets of this size were returned to the pelletizer for coating with the shell material which consisted of a mixture composed of 48% T-64 tabular alumina, 32% A-16 SG alumina powder, and 20% Iowa limestone. As the drum loaded with pellets revolved, the coating material was added gradually while the pellets were sprayed with a dilute lignin solution. Once coated, the pellets were tumbled for 2.0 h more as they were sprayed intermittently with a dilute lignin solution to consolidate the coating and to increase the final calcined strength. The coated pellets were screened subsequently, and pellets of the desired size were then calcined in air at 1373 K for 2.0 h to partially sinter the shell material. Calcination also converted pellet cores derived from limestone into CaO , but it only dehydrated the plaster-based cores. Therefore, cores containing CaSO_4 were treated by a cyclic process conducted at 1323 K which exposed the material to reduction with 9 vol. % H_2 and then to oxidation with 13 vol. % O_2 . The cycle was repeated until 98% or more of the CaSO_4 was converted into CaO .

The absorption characteristics of a pellet were determined by using a thermogravimetric analysis (TGA) system to measure the gain in weight over time of the pellet exposed to a dilute stream of

H₂S at a preselected temperature. For this determination a single pellet was suspended in a quartz basket from an electrobalance so that it could be weighed continuously as it was treated with a gas mixture inside a vertical tubular reactor. The reactor temperature was controlled by a surrounding electrically heated furnace. The gas mixture was supplied to the 2.5-cm diameter quartz tubing reactor at a rate of 500 cm³/min. measured at room temperature and pressure. The mixture was prepared by combining measured streams of H₂S, H₂ and N₂ drawn from high pressure gas cylinders. The H₂S and H₂ were technical grade while the impurity content of the N₂ did not exceed 50 ppm.

To regenerate a sorbent pellet after it had been largely converted to CaS, the pellet was left suspended in the tubular reactor, and as nitrogen was passed through the reactor, the temperature was increased to 1323 K. The pellet was then treated by a cyclic process which involved oxidation with 13 vol. % O₂ followed by reduction with 9 vol. % H₂ (Jagtap and Wheelock 1996; Wheelock 2000). The cycle was repeated until the pellet weight approached a constant value.

Project Description

The present project is an outgrowth of a preceding project which showed that a promising sorbent for desulfurizing hot coal gas could be made by first pelletizing pulverized limestone and then coating the pellets with hydraulic cement (Wheelock et al. 2000). The best coating was made with a calcium aluminate cement designed for high temperature applications. The pellets were capable of absorbing relatively large amounts of H₂S at high temperature (e.g., 1153 K) and were readily regenerated by an alternating cycle of oxidation and reduction. However, the pellets did suffer some loss in reactivity when subjected to repeated loading and regeneration. On the other hand, the advantage of encasing a highly reactive but weak core material in a porous shell of stronger material was clearly shown.

The present project was undertaken to develop further the core-in-shell pellet concept so as to achieve the overall goal of creating a durable, reusable sorbent which can be repeatedly loaded and regenerated without a great loss in reactivity. Soon after the work was started a better shell material was found which consists of a sinterable mixture made with 80% alumina particles of different sizes and 20% limestone particles. Shells made with this composition and calcined at 1373 K are relatively strong while remaining porous. They also withstand repeated cycling of temperature and gas composition. It was also discovered that good pellet cores can be made of plaster of Paris as well as limestone. Furthermore, it was found that the plaster-based cores have greater green strength than the limestone-based cores which facilitates subsequent screening and coating operations. Of course, converting the CaSO₄-based cores to CaO requires an additional treatment step involving several cycles of reduction and oxidation. Moreover, the green strength of the limestone cores can be improved somewhat by incorporating 10% alumina powder in the material.

A number of core-in-shell pellets were prepared with the improved shell material to study the effects of shell thickness, core material, and usage conditions on sorbent performance (Akita, Jr., et al. 2002). When the calcined pellets were tested subsequently, it was observed that the crushing strength of the pellets is directly proportional to shell thickness for pellets having the same core diameter. It was also observed that the reaction of H₂S with the pellets is rapid and directly proportional to H₂S concentration. The rate of reaction did not appear to be affected

greatly by shell thickness or temperature in the range of 1113 to 1193 K. However, the rate was more rapid for plaster-based pellets than for limestone-based pellets having cores made with 10% alumina. On the other hand, an absorption test of bare pellets cores which had not been calcined at 1373 K indicated no difference in the rate of reaction of the two materials. Therefore, the lower rate exhibited by the calcined limestone-based, core-in-shell pellets seemed due to a reaction of CaO with alumina in the core. When the core-in-shell pellets were subjected to several cycles of absorption and regeneration, the limestone-based pellets always suffered a significant loss in reactivity, whereas the plaster-based pellets did not appear to suffer a similar loss. The loss in reactivity was also observed with pellet cores made entirely of pure CaCO₃.

Since the preceding results indicated an advantage for plaster-based pellet cores, the advantage had to be verified and its cause determined. Furthermore, since a very impure plaster of Paris had been used for the preceding work, the possibility that the impurities may have been responsible for the better results had to be considered. Therefore, plaster of Paris with a calcium sulfate hemihydrate content in excess of 99% was selected for further experiments. Also to reduce experimental error, a more refined experimental approach was adopted. A special effort was made to produce smooth pellet cores for coating with shell material. Also to inhibit H₂S decomposition during sorbent testing, hydrogen was added to the gas mixture. The results of a number of experiments conducted with these refinements are reported below. Of course, more work remains to complete the development of a useful material.

Results

The results of a typical determination of the absorption and regeneration characteristics of a limestone-based pellet core are presented in Figure 1. At the outset the pellet consisted almost entirely of CaCO₃, and the material was first decomposed by heating it in a stream of nitrogen. The resulting pellet of CaO was then subjected to four cycles of sulfidation and regeneration. During the sulfidation phase of each cycle, the pellet gained weight as it was treated at 880°C (1153 K) with a gas mixture containing 1.0 vol. % H₂S, 24 vol. % H₂, and 75 vol. % N₂. After 20 min. of absorption, the gas was changed to pure nitrogen, and the temperature was raised to 1050°C (1323 K) for regeneration. The sorbent was regenerated by a cyclic process of oxidation and reduction which involved treating it with a stream of nitrogen which contained 13 vol. % O₂ for oxidation and 9 vol. % H₂ for reduction. The sorbent was fully regenerated after three cycles.

These results differed from those obtained previously without the inclusion of hydrogen in the sulfidizing gas mixture in that the pellet weight increased slightly during the transition from sulfidation to regeneration, whereas before in the absence of hydrogen the apparent pellet weight had decreased noticeably. The previously observed decrease in weight seemed due to the vaporization of elemental sulfur deposited on the upper, cooler portion of the quartz rod that supported the quartz basket containing the sorbent pellet.

The results of the preceding determination are also shown in Figure 2 together with the results of a similar determination made with a pellet core derived from pure plaster of Paris. For this comparison both the percent gain in weight and the corresponding conversion of CaO to CaS are shown for each sulfidation cycle. It can be seen that both pellets displayed similar absorption characteristics, although the plaster-based pellet experienced both a larger conversion and gain in weight than the limestone-based pellet during each sulfidation cycle. Consequently, the plaster-

based pellet was more reactive. Both pellets underwent the greatest gain in weight and conversion during the second sulfidation cycle. Thereafter, there was a gradual decline in both weight gain and conversion.

The absorption characteristics of another plaster-based pellet core were determined for 20 absorption and regeneration cycles, and the results are shown in Figure 3. For this determination the hydrogen concentration during sulfidation was reduced to 12 vol. %. Compared with the results of the previous pellet core sulfidized in the presence of 24 vol. % H_2 , the results seemed slightly worse. Because of the time required, the 20 cycles were spread over five days. At the end of each day the regenerated pellet was removed from the reactor and stored overnight in a desiccator. When the pellet was returned to the reactor, it was always less reactive during the first sulfidation cycle than during the next cycle which suggests that it either underwent a structural change on cooling or adsorbed a gas while outside of the reactor. Of more interest is the gradual decline in conversion and weight gain from cycle to cycle when the first cycle of each day is excluded. While the initial rate of decline was fairly steep, the rate of decline was very low by the end of 20 cycles so the reactivity of the sorbent appeared to approach a constant value. Of further interest is the behavior of the material during the first sulfidation cycle of each day. For the first three days the initial reactivity of the material declined, but then for the next two days it increased inexplicably. Overall, the results suggest that the sorbent was approaching a very stable form where the reactivity would not be affected by taking the sorbent out of service and later returning it to service.

The results presented in Figure 3 differ in one important respect from those obtained previously with pellets made from impure plaster of Paris (Akiti, Jr. et al. 2002). Pellets made from such material did not seem to suffer an apparent loss of reactivity over several cycles of sulfidation, at least in the absence of hydrogen.

To see the effect of extending the sulfidation time on CaO conversion, several different plaster-based, pellets cores were treated at 880°C (1153 K) with different H_2S concentrations while holding the hydrogen concentration at 24 vol. %. The results achieved during the second sulfidation cycle are reproduced in Figure 4. It is apparent that it becomes impractical to convert much more than 70-80% of the CaO to CaS because the rate of conversion becomes very slow beyond this level of conversion, especially with a smaller concentration of H_2S . The rapid decline in the rate of conversion at higher levels of conversion indicates that complete conversion of the CaO can never be achieved because some fraction of the CaO is unavailable due to pore closure or plugging.

For a core-in-shell pellet, the quantity of CaO available for reaction is also determined by the relative proportions of core and shell materials. For a typical core-in-shell pellet with a core diameter of 3.7 mm and shell thickness of 0.30 mm, the core volume is 64% of the total volume. The core mass is an even smaller fraction of the total pellet mass because the density of the core is smaller than the density of the shell. Consequently when a core-in-shell pellet is sulfidized, the gain in weight as a percentage of total pellet weight is considerably smaller than the percent gain in weight of a bare core. This effect can be seen in Figure 5 where the results achieved during the second sulfidation cycle are presented for two bare cores and for two core-in-shell pellets. After 50 min. of sulfidation, the average gain in weight of the bare cores was 20%, while

the average gain in weight of the core-in-shell pellets was 4.3%. Part of this difference may have been due to the diffusional resistance of the pellet shell which could have contributed to a lower overall rate of reaction for the core-in-shell pellets.

The effect of shell thickness is further indicated by the results presented in Figure 6 for four different core-in-shell pellets. Among different pellets, the core diameter ranged from 3.5 to 3.9 mm, and the shell thickness from 0.30 to 0.76 mm. The pellet with the smallest core diameter had the thickest shell so that its core volume was only 34% of the total pellet volume. For the two pellets with the thinnest shells, the core volume represented 64% of the total pellet volume. This difference could have accounted for much of the observed difference in weight gain. However, some of the difference may also have been due to the effect of shell thickness on diffusional resistance.

Application

Various applications are foreseen for the fully developed, calcium-based, core-in-shell sorbent. The material would be well suited for desulfurizing hot coal gas. A previous thermodynamic analysis showed that the gas produced by a typical air- and steam-blown coal gasifier operating at 20 atm. can be 95% desulfurized by CaO under equilibrium conditions over a temperature range of 1043 to 1673 K (Westmoreland and Harrison 1976). Another analysis showed that the H₂S content of gas produced by a Shell entrained flow gasifier can be reduced to 20 ppmv by such a material at 30 bar and over a temperature range of 1088 to 1118 K (van der Ham et al. 1996).

Since a core-in-shell sorbent can be made very durable, the material lends itself to more than one form of gas cleaning. For example, it could be used as a filter medium for removing particular matter, and, therefore, it could be used to simultaneously remove H₂S and dust from the same hot gas stream.

Future Activities

Work on sorbent improvement will continue with the goal of developing a material which suffers little loss in reactivity or absorption capacity over many cycles of loading and regeneration. To achieve this goal it may be possible to take advantage of the apparent difference in results observed with different grades of plaster of Paris or to utilize known sintering inhibitors. Consideration will also be given to less costly materials for the pellet shells. In addition, consideration will be given to the development of a kinetic model which represents the reaction system.

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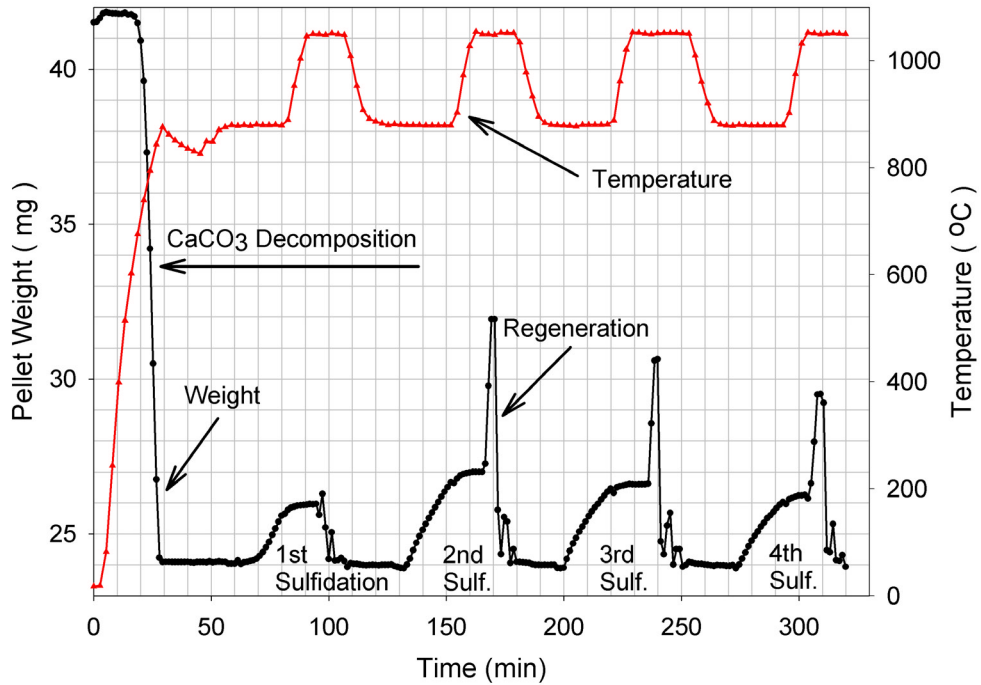


Figure 1. Sulfidation and regeneration characteristics of a limestone-based pellet core using 1.0% H₂S and 24% H₂ for sulfidation at 880°C.

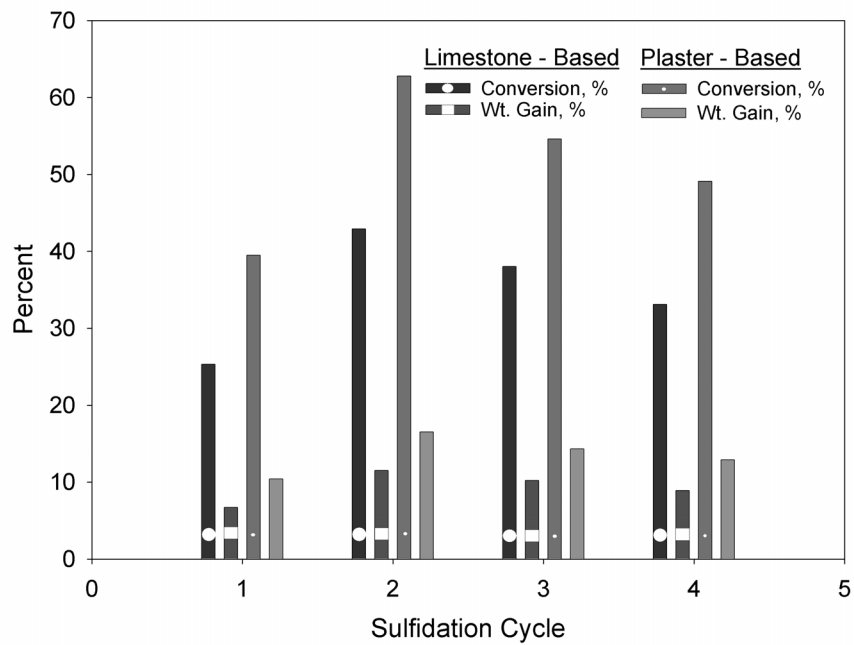


Figure 2. Results of four, 20 min. sulfidation cycles applied to both limestone-based and plaster-based pellet cores. Sulfidation conditions: 1.0% H₂S, 24% H₂, 880°C.

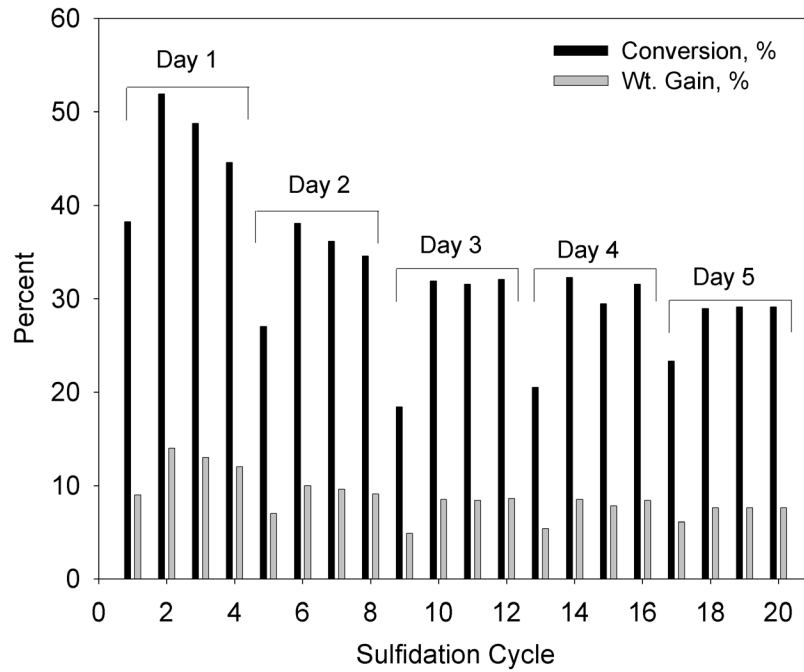


Figure 3. Results of a multicycle sulfidation test in which a plaster-based pellet core was sulfided for 20 min. during each cycle with 1.0 H₂S, 12% H₂ at 880°C.

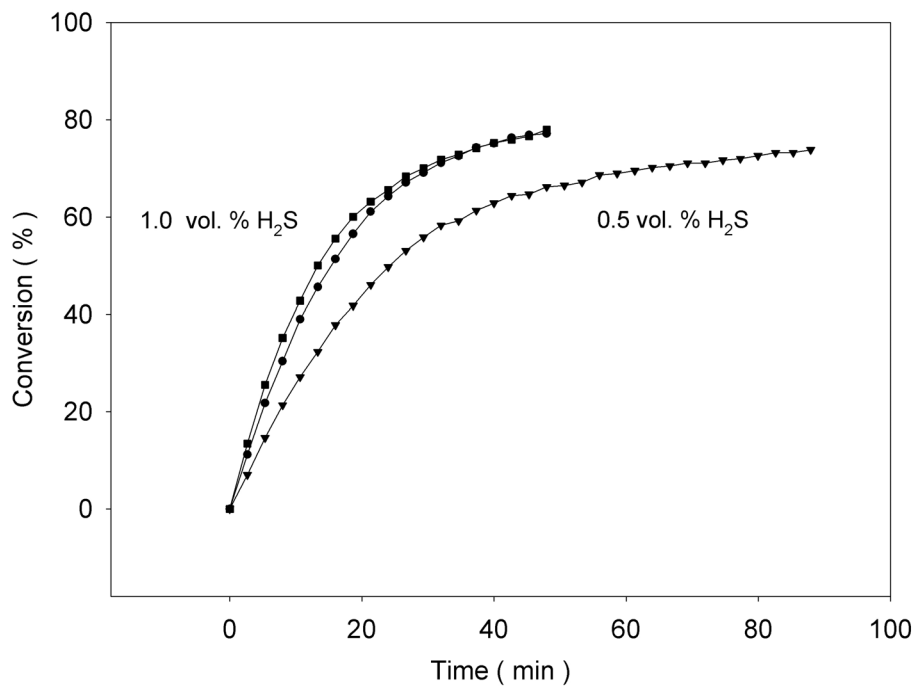


Figure 4. Results of sulfiding plaster-based pellet cores at 880° using 24% H₂ and different H₂S concentrations.

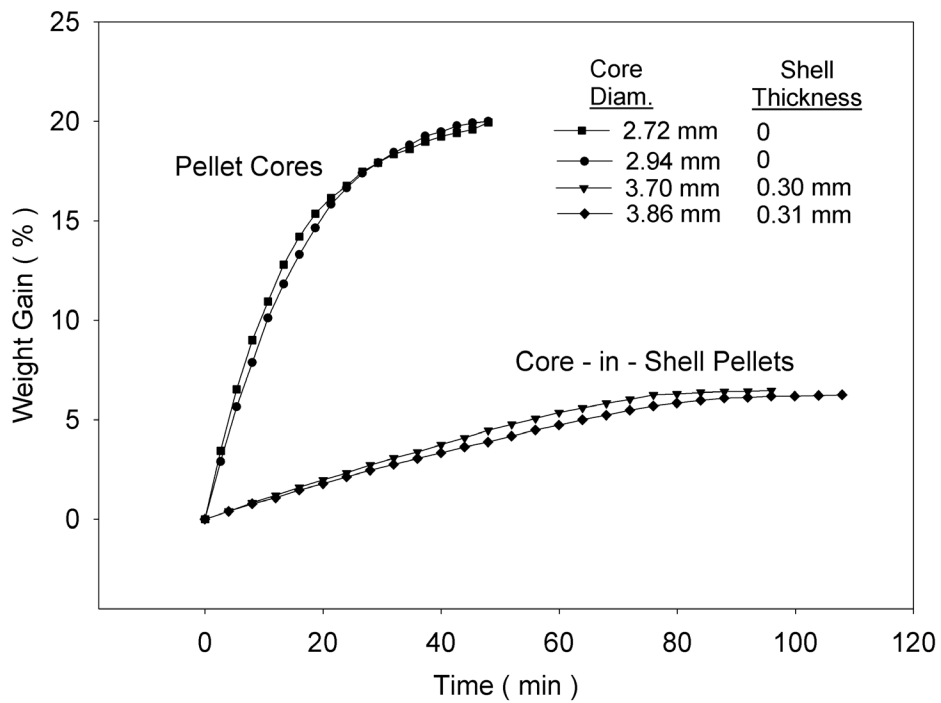


Figure 5. Results of sulfiding plaster-based pellet cores and core-in-shell pellets with 1.0 H₂S, 24% H₂ at 880°C.

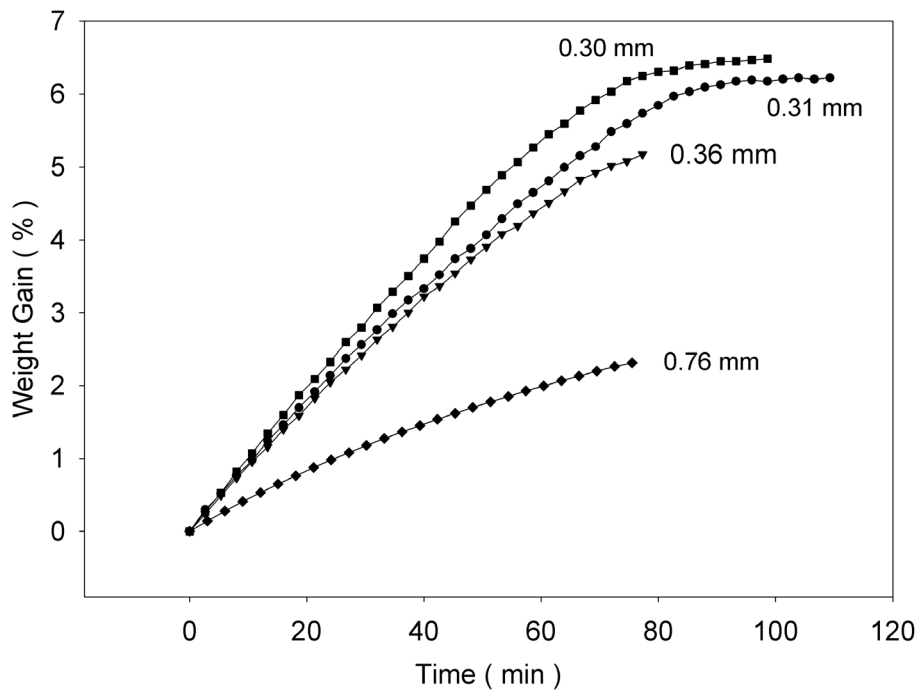


Figure 6. Results of sulfiding plaster-based, core-in-shell pellets with the indicated shell thickness using 1.0% H₂S, 24% H₂ and 880°C.