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EXPERIMENTAL TEST
OF
GAS HEAT TRANSFER SYSTEM
FOR
HYDROXIDE HEAT STORAGE

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MASTER

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By
G. ERVIN

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ABSTRACT

In the development of a heat storage system based on inorganic hydroxide-oxide chemical transitions, the method of transferring heat into and out of the hydroxide storage material is of prime importance. This report presents the results of a series of tests, using circulating gas as a means of heat transfer. On the basis of these results, it is concluded that circulating gas is a technically feasible concept, using steam as heat transfer fluid and using the chemical in the form of a fixed bed of porous granules.

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I. INTRODUCTION

An experimental development of a heat storage method, based on inorganic hydroxide-oxide reversible chemical transitions [such as $\text{Mg}(\text{OH})_2$ - MgO], is in progress. Heat is stored by raising the temperature of the hydroxide to its decomposition temperature, in order to drive off water and convert the hydroxide to oxide. The heat of hydration can then be recovered from the oxide by the addition of water. Because both the hydroxide and oxide are solids of very low thermal conductivity, heat transfer is a limiting property in the design of a practical system. In general, the material must be in thin layers; that is, there must be only short distances through which heat is to be conducted. This condition is also desirable from the standpoint of allowing water vapor to enter and leave the material as it is cycled.

There are a number of ways that can be visualized for transporting heat into a bed of powdered material or into a porous solid. The heat can be transferred by conduction through metal fins or rods inserted in the powder, by a multiplicity of heat pipes embedded in the material, by circulating a fluid through pipes embedded in the material, or by direct contact of the material with a gas. Still another concept is to convey the material in some way through a heated chamber. Each of these concepts has its own problems and drawbacks, as well as advantages. The present report deals with studies of heat transport by direct contact of the material with a circulating gas. The purpose of these studies was to evaluate gas circulation as a basis for getting heat energy into and out of a heat storage device.

In the application to solar heating, for example, the gas is pumped through the receiver of a solar concentrator, where it is heated to a temperature above the decomposition temperature of the hydroxide, and thence through the bed, transferring the needed heat of dehydration in the form of the sensible heat of the gas. Since this method requires that large volumes of gas be circulated, the pressure drop through the system must be kept low in order to avoid significant energy loss for pumping. It is also necessary to contain the material in a way that will avoid entrainment of fine particles by the circulating gas.

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Figure 1. Schematic of Gas Circulating Apparatus for Test of Mg(OH)_2 -MgO Solar Heat Storage System

II. ANALYTICAL STUDIES AND EQUIPMENT DESIGN

A. ANALYSIS

The performance of a gas circulating system for dehydrating and hydrating was analyzed, and the results used to design an experimental rig holding 5 to 15 kg of $\text{Mg}(\text{OH})_2$ with calculated reaction times in the neighborhood of 4 h. The analysis was given in a previous report.* Besides system design, the report dealt with the problem of the fraction of the heat delivered from the solar absorber to the circulating gas which can be stored in the chemical, compared with that delivered directly to the load. It was shown that the theoretical maximum of 42% could be approached by using pure steam, and absorber temperatures substantially above the equilibrium decomposition temperature of 375°C .

Another reason for using pure steam is that the use of air-steam mixtures for hydration will result in long hydration times, because air will blanket the pores of the oxide and prevent free access of water vapor.

B. APPARATUS DESIGN AND FABRICATION

A schematic diagram of the apparatus is shown in Figure 1. The test apparatus employed an electric heater in place of the solar energy collector indicated in the sketch. Gas was circulated by the blower through the heater, through the bed of chemicals in the storage vessel, through the regenerator to the condenser (heat sink) and water tank, and then back through the regenerator to the heater. The regenerator is necessary with air-steam mixtures to prevent dumping most of the circulating heat to the heat sink or load. In an actual system, using pure steam, the regenerator would not be necessary. Under these circumstances, only a portion of the steam would be condensed during the cycle, and the major circulating stream would not be cooled.

The apparatus actually built followed the design shown in Figure 2. The piping is carbon steel, and is insulated with Kaowool and wrapped with heater cord in order to balance the heat loss to the surroundings. The heater is a 3-kW hairpin-shaped Nichrome resistor with disc-shaped fins. The pump is a

*G. Ervin, D. K. Chung, and T. H. Springer, "A Study of the Use of Inorganic Oxides for Solar Energy Storage for Heating and Cooling of Buildings," AI-75-63, NSF/RANN/SE/GE-44/FR/75/2 (October 1975)

9162-5402

Figure 2. Engineering Drawing of Gas Circulating Apparatus

positive displacement type with a capacity of 100 scfm, powered by a 3/4-hp motor with variable clutch drive. There was a rotometer with capacity of 14 scfm. The gas flow during the tests was typically 4 to 7 scfm. Photographs are shown in Figures 3 and 4.

C. OPERATING PROCEDURE

The purpose of this experiment was to measure the extent of reaction, dehydration or hydration, as a function of time, for various containment geometries. Runs were made with three geometries — two, in which the chemical $[\text{Mg}(\text{OH})_2]$ was in thin layers in a porous-walled containment structure; and a third, in which a granular form of the chemical was contained in a fixed bed.

Operation was in air or steam, or mixtures of these. The flange seals were not sufficiently leaktight to permit operation in high-purity steam, but at pressures above 1×10^5 Pa (1 atm) the air contamination was probably <1%. The system was filled with steam by evacuating it, and then generating steam by boiling water either from the water reservoir or from water run from the reservoir into the heater chamber.

For each experiment, the reaction chamber was charged with $\text{Mg}(\text{OH})_2$ which was dehydrated by circulating hot gas through it, and water was collected in the water reservoir as it condensed in the condenser above the reservoir. There was, unavoidably, about a 2-h heating up period. Moreover, the various parts of the bed of $\text{Mg}(\text{OH})_2$ heated up at different rates. Thus, the runs were not isothermal with time, nor with position in the bed.

Hydration also was not isothermal because the circulating steam caused temperature gradients throughout the reaction chamber, and the release of the heat of hydration caused temperatures to rise continually until hydration was nearly complete.

The principal information obtained from these experiments was a rough measure of the times needed for complete dehydration or hydration for each of the different geometries, and the comparison between steam and air as heat transfer media. Crude heat balances were also attempted; but from a design point of view, a heat balance on this equipment is not of much significance, because the equipment is strung out, rather than compact, and the small capacity also results in heat losses that are large relative to the quantity stored.

Figure 3. Gas Circulating Test Apparatus
Without Insulation

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Figure 4. Reaction Chamber and Regenerator Sections of Insulated Gas Circulating Test Apparatus

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III. EXPERIMENTAL RESULTS

A. PIN-TYPE CONFIGURATION

Reagent grade $\text{Mg}(\text{OH})_2$, in the form of a fine powder, was packed in the annular space in 2.54-cm (1-in.) diameter stainless tubes having 0.64-cm (1/4-in.) diameter tubes axially through their centers. The small central tubes were made from stainless steel wire cloth, 200 x 1400 mesh, with a nominal opening of $5\ \mu$. There was a bundle of 37 of these tubes, as shown in Figure 5, and the weight of $\text{Mg}(\text{OH})_2$ was 23.8 kg (10.8 lb).

8402-4003

Figure 5. Open Top of Reaction Chamber, Showing 37-Tube Bundle of Tubes Containing $\text{Mg}(\text{OH})_2$ Powder

Dehydration was performed with air as the circulating gas. The results given in Table 1 show that decomposition was 90% complete in ~ 3 h at temperatures mostly below 375°C , which is the temperature at which the equilibrium partial pressure of water over $\text{Mg}(\text{OH})_2$ is 1×10^5 Pa (1 atm), according to published data. This finding agrees with expectations, because the partial pressure of water in the circulating air is low, certainly $< 1 \times 10^4$ Pa (0.1 atm), because water is continually condensed out as the air circulates through the condenser.

TABLE 1
GAS CIRCULATING APPARATUS
PIN-TYPE CONFIGURATION

Time (h)	Temperature ($^{\circ}\text{C}$)	Reaction Completion (%)
Dehydration, Air at 7 scfm		
0.58	316	10
0.83	327	21
1.00	332	29
1.67	357	61
2.25	367	77
2.75	380	88
3.25	382	91
3.75	390	93

A crude heat balance on this experiment shows the following:

Heater power = 1580 W

Heater input in 3 hr = 16.2×10^6 J (16,200 Btu)

Heater needed for 90% dehydration of 6155 g $\text{Mg}(\text{OH})_2$ = 7.425×10^6 J
(7425 Btu)

Less than half of the heat was used for the heat storage reaction, a substantial additional fraction was used to heat up the material and the apparatus, and the balance was lost through the insulation. Insulation losses will be much less in a full-scale apparatus, because of a much larger ratio of storage material to outside surface.

9162-5403

Figure 6. Cross Sections of Reaction Chamber With $Mg(OH)_2$ Powder in Concentric Cylinders

Hydration of the MgO in the reaction chamber was then attempted in order to complete the cycle and recover the absorbed heat. However, it was found that hydration, using air as a carrier for water vapor, was very slow, requiring more than 24 h. The low rate is believed to be due to blockage of water vapor transport by a blanket of air which fills the spaces in the MgO bed, after partial hydration has depleted it of water vapor. In addition, hydration was inherently limited in this experiment since the 2.54-cm (1.0-in.) diameter tube was not made of wire cloth as it would normally be in a practical system. The metal tubing was used as an expedient to get early data on dehydration characteristics.

B. CONCENTRIC CYLINDERS

For the next experiment, the reaction chamber space was packed more densely with $\text{Mg}(\text{OH})_2$ by using a set of four hollow concentric cylindrical containers that were made of wire cloth to retain the powder, but that provided permeability to water vapor. These nesting cylinders were double-walled, to provide 1-in.-thick packing of $\text{Mg}(\text{OH})_2$ powder. Cross sections of this configuration are indicated in Figure 6. Channels between containers were formed by a helical winding of 0.16-cm (1/16-in.) diameter wire.

The experimental results are indicated in Tables 2 and 3. The configuration just described is designated as close packing in Table 2, and it is evident that both dehydration and hydration were very slow. This is attributed to poor contact between the circulating gas and the $\text{Mg}(\text{OH})_2$, due to partial collapse of the channels between containers. A second trial was then made using steam instead of air, and removing alternate containers from the nesting set, thus leaving very wide channels, over 1 in. wide, between the remaining containers. These changes caused faster reactions, as shown in Table 3, but the void fraction in the reaction chamber was very high.

The experiment of Table 3 was significant in that this was the first experiment in which steam was used to dehydrate $\text{Mg}(\text{OH})_2$. Another point to note in Table 3 is the rise in temperature of the $\text{Mg}(\text{OH})_2$ during the hydration part of the cycle, due to release of the heat of hydration. Nevertheless, the rate of reaction was disappointingly low, considering the very open configuration.

The final experiment was performed with concentric cylinders, in which the space was filled to the highest fraction possible, and yet adequate channels for gas flow were provided. Spacing between containers was established by wrapping

TABLE 2

GAS CIRCULATING APPARATUS
CONCENTRIC RING CONFIGURATION - CLOSE PACKING

Time (h)		Temperature Range (°C)	Volume Water Collected (ml)	Rate (%/h)
Dehydration, Air*				
2.5		274 - 361	455	4.2
3.3		323 - 410	607	6.9
3.8		235 - 381	633	7.0
4.8		272 - 400	708	2.7
6.8		311 - 422	1011	5.5
13.0		342 - 436	2099	4.4
15.0		369 - 433	2276	3.2
21.4		401 - 447	2782	2.9
	Steam Pressure [kPa (psia)]		Volume Water Absorbed (ml)	
Hydration, Steam*				
2.0	-	210 - 219	556	10.1
2.8	-	82 - 101	859	13.8
3.8	108 (15.7)	94 - 121	1061	7.3
6.3	112 (16.2)	99 - 122	1415	5.1
7.4	41 (5.9)	74 - 82	1921	16.7
8.6	88 (12.7)	91 - 104	2275	10.8
9.6	71 (10.3)	88 - 113	2427	5.5

*Air and steam flow rates were nominally 6 scfm

TABLE 3
GAS CIRCULATING APPARATUS
CONCENTRIC RING CONFIGURATION - OPEN PACKING

Time (h)		Temperature Range (°C)	Volume Water Collected (ml)	Rate (%/h)
Dehydration, Steam*				
1.1		307 - 366	441	28.2
2.3		338 - 410	910	27.5
4.8		435 - 455	1215	8.6
	Steam Pressure [kPa (psia)]		Volume Water Absorbed (ml)	
Hydration, Steam*				
0	105 (15.2)	172 - 199	0	-
1.75	108 (15.7)	194 - 214	304	12.2
4.4	108 (15.7)	225 - 245	910	16.1
6.25	100 (14.7)	225 - 240	1366	17.3

*Steam flow rates were nominally 6 scfm

them with 0.32-cm (1/8-in.) diameter helix made of 0.16-cm (1/16-in.) diameter wire. The spacing between turns of the wrapping was about 2.54 cm (1 in.). Even so, the gas flow, as observed qualitatively, was unevenly distributed over the cross-section of the bed, and the poor efficiency of heat transfer was borne out by the relatively long dehydration time of 7 h. Uneven gas flow was even more evident for the hydration step, which was slow and incomplete. Data for these runs are shown in Table 4.

TABLE 4
GAS CIRCULATING APPARATUS
POWDERED $\text{Mg}(\text{OH})_2$ IN CONCENTRIC NESTING CYLINDERS

Cycle	Elapsed Time (h)	Flow Rate (liter/s)	Steam Pressure (kPa)	Temperature Range (°C)	Reaction Completion (%)
1st Dehydration	7.3	3.3	130	350 - 510	100
1st Hydration	2.5	3.3	105 - 170	65 - 130	53
2nd Dehydration	6.3	2.8	135 - 175	365 - 455	80
2nd Hydration	5.0	2.8	130	90 - 115	40

TABLE 5
PRESSURE DROP AND PUMPING POWER OF A FIXED BED
HEAT STORAGE VESSEL SYSTEM

Material:	Mg(OH) ₂		
Weight:	1135 kg (volume of bed = 1100 liter)		
Total Heat Storage Capacity:	8.9 x 10 ⁸ J		
	260 kWh(t)		
	32 kW for 8 h		
Dehydration Time:	8 h		
Heat Transfer Fluid:	Pure steam		

Steam Pressure (atm)	Inlet Temperature		
	427°C (800°F) [ΔT = 28°C (50°F)]	454°C (850°F) [ΔT = 56°C (100°F)]	510°C (950°F) [ΔT = 94°C (170°F)]
1	Bed ΔP (kPa)	28	8
	Pipe ΔP (kPa)	8	2
	Blower W (kW)	171	23
2	Bed ΔP (kPa)	14	4
	Pipe ΔP (kPa)	4	1
	Blower W (kW)	42.8	5.8
4	Bed ΔP (kPa)	7	2
	Pipe ΔP (kPa)	2	0.5
	Blower W (kW)	10.7	1.5

TABLE 6
GAS CIRCULATING APPARATUS FIXED BED OF
SILICATE-BONDED GRANULES

Cycle	Elapsed Time (h)	Flow Rate (liter/s)	Steam Pressure (kPa)	Temperature Range (°C)	Reaction Completion (%)
1st Dehydration	3.0	2	130 - 150	345 - 410	71
1st Hydration	2.8	3	190 - 210	105 - 120	80
2nd Dehydration	3.0	2	165 - 190	340 - 495	75
2nd Hydration	4.0	2 - 4	100 - 190	45 - 180	80
3rd Dehydration	4.75	2	130 - 145	335 - 500	80
3rd Hydration	2.0	0	100 - 170	65 - 250	80
4th Dehydration	3.75	2	130 - 145	300 - 470	67
4th Hydration	2.0	2	100 - 130	50 - 185	80
5th Dehydration	2.5	2	125 - 145	300 - 530	65

C. FIXED BED CONTAINMENT

The most efficient heat transfer for the gas circulation concept would be achieved by flow of the gas through a bed of the solid particles, rather than in channels between porous-walled vessels which contain the powder. There are two alternative modes — fixed bed, or fluidized bed. Brief trials of each of these modes, using fine $\text{Mg}(\text{OH})_2$ powder, showed that entrainment of the fines in the circulating gas stream would be very substantial, and would require particle separation devices, which are an undesirable complication.

It was then found that the fines could be eliminated by the use of an inorganic binder to make coarse granules. Sodium silicate is a cheap material, widely used as an inorganic cement. Addition of a commercial solution of sodium silicate to $\text{Mg}(\text{OH})_2$ powder, in the proportion of 8% of the dry silicate by weight, resulted in granules whose size could be controlled in the range of about 1.27-cm (1/2-in.) diameter and finer, and with a very small fraction below 100 mesh. This is a size range that can be packed in a fixed bed, and can accommodate moderate gas flows with low pressure drop and no particle entrainment in the gas stream. Tests in another apparatus showed that these granules could be dehydrated and hydrated rapidly, and that there appeared to be no tendency to generate fines as a result of cycling between the hydroxide and oxide forms; however, the latter observation is based on only five cycles. Calculations (Table 5) showed that pumping energy associated with such a fixed bed can be reduced to a value <2% of the stored energy by the proper choice of parameters. The use of 2.54-cm (1-in.) diameter granules, a bed geometry of 122-cm (4-ft) diameter by 91-cm (3-ft) high, and a pressure of 8×10^5 Pa (8 atm) steam, would permit operation at (427°C (800°F) with <2% pumping energy.

The reaction vessel of the gas circulating apparatus was fitted with a fine screen near the bottom, and was charged with 8.7 kg (19.2 lb) of silicate-bonded $\text{Mg}(\text{OH})_2$ granules. The arrangement is indicated in Figure 7. The material was put through four dehydration and hydration cycles, data for which are given in Table 6. In general, dehydration times were 3 to 4 h, and hydration times somewhat shorter. The system was opened up after the fifth dehydration, and there was no evidence that the granules were breaking down into fines. Of course, many more cycles will be needed for a good test of this behavior.

The pressure drop through the fixed bed of granules was not measured accurately in these experiments, but appeared to be less than 7 kPa (1 psi), in agreement with theoretical calculations of pressure drop in packed beds.

Figure 7. Vertical Cross Section of Reaction Chamber Filled With $Mg(OH)_2$ Granules

IV. CONCLUSIONS

The experimental testing program described in this report was aimed at an evaluation of the concept of heat transfer by means of the sensible heat in a gas and applied to the operation of a solar heat storage system based on the $\text{Mg}(\text{OH})_2$ - MgO transformation. The apparatus was designed for experimental testing, rather than as a compact model of a practical system. It provided semiquantitative information on the validity of the concept, on dehydration and hydration rates, on pressure drops in the circulating gas, and on operating difficulties to be expected. Heat losses were such that little information on heat balances could be obtained.

The results show that the overall concept of gas heat transport is valid, and that reasonable dehydration and hydration times, in the neighborhood of two hours each, can be achieved, if the geometry of containment of the $\text{Mg}(\text{OH})_2$ - MgO material provides good contact between the circulating gas and the chemical. Containment of powdered chemical in porous-walled chambers gave only marginal performance, and only if relatively wide gas channels between chambers were provided. The best geometry, by far, was a fixed bed of granular $\text{Mg}(\text{OH})_2$. The granules can be formed by bonding $\text{Mg}(\text{OH})_2$ powder with an inorganic cement, made from a commercial grade of sodium silicate. The cement has been shown, in other tests described in periodic reports on this program, to survive many cycles without change in the performance of the granules.

Steam appears to be a better choice than air for the circulating gas. Superheated steam at 1 to atm works very well for dehydration at 300 to 500°C, and nearly pure steam is essential for rapid hydration. If an appreciable percentage of air is present, hydration becomes very slow.

Proper choice of granule size and fixed bed geometry will result in pressure drops small enough to keep the circulating pump energy a small percentage of the energy stored.