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HIGH TEMPERATURE COMPOSITE THERMAL STORAGE SYSTEMS FOR INDUSTRIAL APPLICATIONS

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ABSTRACT

An advanced, thermal energy storage (TES) subsystem is being developed by the Institute of Gas Technology (IGT) which employs composite phase change material (PCM)/sensible heat media (CompPhase™). This medium/subsystem is amenable to high temperature thermal storage applications such as industrial reject/process heat recovery and utilization, off-peak utility, and solar thermal and solar dynamic space power systems. The CompPhase™ concept allows for direct contact heat exchange between the latent/sensible storage media and compatible working fluids. A number of potentially significant TES system performance and cost advantages are thereby offered over conventional tube intensive indirect contact molten-salt latent-heat-based storage subsystems.

Materials processing, stability analysis, modeling and development efforts are progressing on composite systems from 390° to 1750°F. Performance testing of a bench-scale packed-bed unit with ~50 lbs of pellets has accumulated over 6000 hours and 200 thermal cycles, with excellent media stability (~.3% weight loss in 1000 hours) and high heat transfer rates (~10,390 Btu/hr discharge heat-removal rate.

Preliminary economic assessments indicate that the projected cost for this advanced subsystem is below the maximum allowable cost for typical high temperature reject heat recovery applications, as well as being ~30% lower in cost than current baseline sensible-heat based TES systems.

INTRODUCTION

The use of phase change materials (PCM) for high temperature thermal storage applications provides a number of desirable features (high volumetric storage capacities, heat availability at rather constant temperature, etc.).[1-4] However, the growth of the solidified phase on the heat transfer surface during discharge (in a molten bath, tube intensive HX) seriously affects the heat transfer rates. Several investigators have tested numerous means to improve the heat transfer characteristics such as scrapers, conductivity enhancers, and various extended fin arrangements without much success. Recent engineering R&D efforts at IGT have demonstrated the technical feasibility of an alternative approach to containing molten carbonate salts that offers the potential for elimination of heat exchanger (HX) tube configurations and operation in direct contact with compatible working fluids. This approach, therefore, represents the possibility for significant cost improvements through elimination of HX tube materials and fabrication cost and reduced containment vessel sizing cost, as well as enhanced thermal performance via direct-contact operation.

COMPOSITE SALT/CERAMIC TES MEDIA CONCEPT

The CompPhase™ composite TES media concept involves retention and immobilization of a phase-change salt (latent-heat phase) within the submicron-sized porous microstructure of a particulate ceramic matrix or porous sintered ceramic body (sensible-heat phase).* The molten salt is retained within the micro-porosity defined by the ceramic network by capillary/surface tension forces. The volume fraction of molten salt that can be retained is determined by the characteristics of the support material (e.g. particle size and relative shape distributions and specific surface area), salt properties (e.g. surface tension and viscosity), and wetting behavior (wetting angle) between the molten salt and ceramic phases. The feasibility of retaining 70 vol. % (or 57 wt. %) of molten carbonates within a ceramic particle matrix at 1650°F has been experimentally demonstrated. Retention of higher volume fractions of liquid may be possible by optimization of ceramic support characteristics and media processing conditions.

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* IGT patent retained. Trademark: CompPhase™.

Immobilization of the molten salt within the porous ceramic microstructure permits operation of the composite media shapes in direct contact with compatible fluids, thus eliminating the cost and heat transfer resistance associated with heat-exchanger tubes required in shell-and-tube HX designs. Such a direct-contact HX design may consist of composite media shapes fabricated as cylindrical pellets, briquettes, spheres, etc. and utilized in a packed-bed arrangement. Alternatively, these composite materials can be formed as brick shapes and stacked in a regular array similar to a brick checkerwork regenerator. Media composition, shapes and sizes can be readily varied to thermally tailor a bed to a given operating temperature swing and optimize heat transfer surface area/volume ratio and bed packing density.

COMPOSITE MEDIA DEVELOPMENT AND TESTING

MATERIALS SELECTION

The ceramic support materials (sensible-heat phase) were selected primarily from metal oxides, aluminates, ferrites, or titanates. The functions of the porous or particulate ceramic phase are to provide stable capillary forces for retention of the molten carbonate phase and to contribute sensible heat to the composite media. The most critical property of the ceramic support material is expected to be its chemical stability in the high-temperature liquid carbonate environment. Significant chemical reaction or solubility of the ceramic in the molten carbonate will affect the long-term salt retention property and structural integrity of the composite. Other selection criteria for the ceramic support materials include specific heat, cost, and the ability to be prepared as fine particulates or micro-porous bodies.

Current industrial-application-targeted phase-change-materials (PCM's) screening for use in CompPhase™ bench-scale testing has emphasized alkali-earth and alkaline earth metal carbonates and their mixtures. The salts are attractive for utilization in this direct-contact TES/HX concept because of their superior high temperature chemical stability, melting points of interest (740° to 1650°F), moderate to high heats-of-fusion (70 to 261 Btu/lb), low cost ($0.04/lb to $1.50/lb), and low vapor pressures in air and other oxidizing gases containing CO_2, O_2, and H_2O.

Emphasis is being given to compositions based on Na_2CO_3 because of its attractive heat-of-fusion (114 Btu/lb), heat capacity (0.40 Btu/lb-°F) and low cost as a technical-grade salt ($0.04/lb). A CompPhase™ medium consisting of ~51 wt % of the carbonate salt of composition 48 wt % Na_2CO_3/52 wt % $BaCO_3$ (m.p. 1330°F) supported by 49 wt % MgO particles is being investigated as a model high-temperature composite TES material.

MEDIA PROCESSING AND FABRICATION

Composite media preparation work has followed a two-pronged approach to maintain continuous interaction between controlled laboratory materials development and commercial production feasibility.

This closely coordinated effort allowed us to move from packed-bed laboratory-scale (0.4 kWh_t) testing of 2.42 lbs of manually cold-pressed pellets to engineering-scale (~7.4 kWh_t) testing of 47 lbs of commercially spray-dried and extruded pellets of the model Na_2CO_3-$BaCO_3$/MgO material through three phases of testing, totalling >6000 hours and >200 thermal cycles.

Originally, composite carbonate/ceramic powders were prepared from aqueous slurries using a spray-drying process, which produces homogeneous, intimately dispersed powder with good flowability and forming characteristics (as those employed in the bench-scale testing above). Spray-drying process procedures were developed for preparation of ceramic supports and composite powders with controlled characterized properties such as chemical composition, specific surface-area of support, particle size and shape distribution, flowability and forming.

The cost of spray-drying, however, was determined to be a big factor for the overall TES media cost. Alternative media processing methods without spray-drying were, therefore, investigated. Initial efforts involved mixing composite powder prepared by vibratory milling of the proper amounts of Na_2CO_3, $BaCO_3$, and MgO powder with a milling aid. No powder-caking was observed during milling (S.A. characteristics of milled powder vs. spray dried). The milled powder was heated to 1472°F in air to melt the carbonate phase and to distribute itself within the MgO particulate matrix. We estimate a savings of 35% in media cost as a result of this process modification. Single pellet stability tests of the dry-milled media at 1472°F (in air) for 600 hours resulted in 1.2% wt loss. These results are comparable to those with pellets obtained from the spray-dried powders.

Finally, a simplified, semi-dry process has been developed which now makes the CompPhase™ media-production scheme amenable to all the mass production steps typically employed in the common brick/ceramic manufacturing industry. It involves a semi-dry-blended composite mixture with low temperature/time drying, direct-forming without additives, and short-term densification firing. Figure 1 depicts this successful evolution of production schemes from those of the controlled-laboratory to the "real-world" (economical) common refractories processing plant.

MEDIA BEHAVIOR AND TESTING

The technical feasibility of this composite approach to high-temperature TES depends largely upon the behavior and stability of the media, which includes: ceramic support capillarity, chemical stability, thermal cyclability, and mechanical strength. The candidate composite media are being evaluated in experiments designed to address and quantify these key technical questions, which will ultimately affect the composites true functionality in any industrial setting.

An engineering-scale TES facility has been designed and constructed for evaluation of the charge/discharge performance of a packed-bed of composite carbonate/ceramic media pellets. The TES unit is of AISI Type 316 stainless steel construction with a 10 mil Inconel 600 liner, and can accommodate a maximum bed volume of 0.7854 ft^3. The bed is charged by a direct-contact electrical resistance air heater (design point: heat 10 SCFM to 1600°F) from the top of the unit, while it is reversibly discharged with 50°F air (7 to 15 SCFM) from the unit's base (typically cycled from an average bed temperature of 1418° to 784°F).

The TESU is adequately instrumented to provide reliable and detailed data for evaluating radial and axial bed temperature distributions, solid/gas heat transfer coefficients, efficiency, flow rates of charge/discharge gases, and pressure drops through the packed media. As mentioned above, 47 lbs of the 51 wt % Na_2CO_3-$BaCO_3$/ 49 wt % MgO pellets (commercially spray-dried and extruded, of 1.18 in diameter X 1.18 in height) were installed into the test unit and subjected to 3 phases of testing, totalling 6030 hours and 206 thermal cycles. The overall testing summary appears in Table 1.

Table 1. BENCH-SCALE TESTING SUMMARY

Phase	Thermal Cycles	Hours	Wt. Loss % Within Phase
I	47	1680	0.3
II	62	1920	1.7
III	97	2430	--
	206	6030	1.6

Post-test analyses revealed that the media retained its high integrity (as seen in Figure 2) with minimal pellet-cracking and no repeated cracking/ crumbling in the instances if a pellet cracked in 2 to 3 pieces. The media's stability was further demonstrated by a total gross pellet weight loss of 1.6%. The measured pellet densities were practically the same, exhibiting a 4.1% decrease from pre- (2.88 g/cm^3) to post-test (2.76 g/cm^3). X-ray diffraction analysis did not reveal any other phases but eutectic Na_2CO_3-$BaCO_3$ and MgO. Pre- and post-test analyses (from combined atomic absorption and CO_2 evolution) appear in Table 2. Analyzed chemical compositions of the pre-test media were consistent with each other; yielding an average of 27.6% $BaCO_3$, 23.0% Na_2CO_3, and 49.3% MgO (see Table 2). Phase III post-test

Table 2. CHEMICAL ANALYSES OF PELLETS THAT UNDERWENT ALL THREE PHASES OF TES PERFORMANCE TESTS

Pellet No.	Sample of Hfo Location in Bed	Na_2CO_3	$BaCO_2$	MgO	$\frac{Na_2CO_3}{MgO}$	$\frac{BaCO_3}{MgO}$
Post-Test-Phase III						
TC-13	Top	17.6	31.9	50.5	0.35	0.63
TC-13B	Above Cntr (3/4 ft)	24.5	27.6	47.9	0.51	0.58
TC-9	Center (1/2 ht)	23.9	25.4	50.7	0.47	0.50
TC-5-7	Below Cntr (1/4 ht)	23.5	25.9	50.6	0.46	0.51
TC-5	Bottom	24.5	25.0	50.3	0.49	0.50
Post-Test-Average:		22.8	27.2	50.0	0.46	0.54
As-Spray-Dried Powder, No. 1		22.9	27.5	49.6	0.46	0.55
As-Spray-Dried Powder, No. 2		23.7	28.4	47.6	0.50	0.60
As-Extruded Pellet		22.6	26.6	50.8	0.44	0.52
As-Sintered Pellet		22.9	27.9	49.2	0.47	0.57
Average:		23.0	27.6	49.3	0.47	0.56

samples were obtained from five height locations along the bed-center. One quarter of each sample was completely dissolved and analyzed. Assuming that there was no loss or migration of MgO, the Na_2CO_3/MgO and $BaCO_3$/MgO ratios of the tested media would reveal the distribution trends of the salt composition. These ratios are included in the table. They indicate a slight Na_2CO_3 depletion from the top-most pellet media. There was no significant Na_2CO_3 loss from media at other locations. The $BaCO_3$/MgO ratio was slightly higher for the top two pellets. (However, precision in $BaCO_3$ analysis is not as fine as that for Na_2CO_3 or MgO; requiring further verification.) The average composition of the five 6030 hour tested pellets are in good agreement with that of the pre-test media and is in line with the accounted small overall weight losses of the media. These results indicate that CompPhase™ Na_2CO_3-$BaCO_3$/MgO media operated at 1490°F or higher as the top pellets in the performance tests will be subject to slight Na_2CO_3 loss and/or salt migration. It also indicates that the Na_2CO_3 lost from the top pellet was not replenished by capillary flow.

The heat flux, Q, from/to the air working fluid to/from the composite media was determined as a function of time for each half-cycle by monitoring the inlet and outlet air temperatures and calculating Q from the expression —

$$Q = \frac{\dot{m}\ C_p\ \Delta T}{A}$$

where

Q = heat flux, Btu/hr-ft^2

$\dot{m}$ = air mass flow rate, lb/h

C_p = heat capacity of air, Btu/lb-°F

ΔT = air temperature differential = $T_{out} - T_{in}$, °F

The heat transfer area used to evaluate this heat flux was defined as the total surface area of all the pellets, which was calculated to be 18.49 ft^2 for Phase I and 15.2 ft^2 (39 lbs) for Phase II testing. The air outlet (inlet) temperature was initially measured at the center of the feed pipe, very close to the unit top and bottom. Discharge outlet delivery temperatures (with 11 SCFM air flow at blower) for the composite are very high, averaging from 1562° to 1157°F compared with 374° to 194°F for a similar salt temperature swing using the molten 48 wt % Na_2CO_3-53 wt % $BaCO_3$ PCM alone in a single heat exchanger tube configuration (6-in. x 3-in. high canister with 1/2 in. HX tube). Cyclic utilization factors were calculated from the bed temperature distributions to be 60% to 70%.

Attempts at computing heat balances between these average heat fluxes and the apparent heat release from the bed (as measured from piece-wise integration using axial and radial bed temperature distributions before and after discharge) indicated supplemental heat contributions to the discharge air working fluid from the external TES piping, containment and insulation. While the main focus of this test set was to assess the materials endurance of the composite medium, heat flux values for the three test phases were recalculated, referencing the air working fluid "delta T" to two thermocouple sets located adjacent to the actual bed "bottom and top." This was done in an attempt to determine that portion of the <u>TES unit's</u> heat flux more appropriately attributable to the composite pellets themselves. These new values appear on Figure 3. This figure plots the <u>mean</u> (from a population of runs at a given flow rate within a specific phase) average-heat-flux at flow rates from 7 to 11 SCFM within Phases I, II, and III. The solid lines are the "TES unit's" heat flux performance, while the dashed lines depict a conservative estimation of the heat flux contributed by the pellets. With the bed heat flux viewed in this manner; general (flow-rate-specific) heat fluxes become apparent across test phases:

Flow Rate, SCFM	Heat Flux, $Btu/hr\text{-}ft^2$
11	325
10	300
8	225
7	180

INDUSTRIAL APPLICATIONS

The advanced media development and TES testing results will provide a significant data-base relevant to a broad range of high-temperature industrial storage applications, including the metallurgical, brick/ceramics and refractories industries. The initially targeted TES application is in the SIC-32 industries (brick, ceramic, clay products, and refractories) which use periodic kilns exhausting high-temperature (482° to 2012°F) flue gases.

Approximately half of the firing kilns in SIC-32 industries are periodic in nature and well-suited to integration with thermal energy storage. Figure 4 shows 1981 levels of fuel consumption in SIC-32 categories. Implementation of TES could result in ~45% energy savings for a typical periodic kiln installation and a total SIC-32 industry annual energy savings of 0.2 quad.[5] Further analyses will be performed to further refine assessments of energy savings, cost-effectiveness, and environmental acceptance of an advanced TES system in this industry category.

Typical operation of a periodic kiln involves a heat-up stage, a soaking stage, and a cool-down stage as depicted in Figure 5. During the first two stages, hot flue-gases can be routed to a TES device; during the cool-down stage; heated air passing over the hot product can also be routed to the TES device. Thus, the TES unit is charged thermally with heated gases that are normally vented to the ambient. Three possible uses of the heat stored in the TES unit are —

1. Preheating of combustion air to 600°F and above.

2. Preheating kiln ware up to 1000°F prior to firing of kiln burners.

3. Greenware drying, utilizing heat from the TES unit in the 100° to 250°F temperature range. All of the energy normally input to the dryers can be obtained from the TES device, thus saving as much as 50% of <u>total plant fuel consumption</u>.

A centrally located TES unit divided into several modules can be designed to accept heat from several sources and reject the heat to other heat-requiring operations within the plant. Figure 6 shows a 2 kiln/1 dryer brick plant incorporating a TES unit consisting of one

TES module per heat-using device. Such a system requires high temperature ductwork and valves, blowers, and a control and instrumentation scheme to optimize heat usage.

Another area where this concept possesses strong potential is in utilities applications involving user (residential and commercial) storage of off-peak electricity for space conditioning. Electrical resistance heaters may be employed to directly charge the composite TES media in space-conditioning "package units" during off-peak hours, while discharge occurs with forced ambient air either in direct contact with an appropriately compatible composite or in contact with the medium's high-conductivity (e.g., Al or Cu) containment canister. The phase-change component's melting point may be varied from 572° to 1470°F by proper selection of the salt composition for such an electrically charged/forced-air discharged space-heating application.

A possible solar application of the concept is in storage for solar Brayton central receiver power systems operating at 1290° to 1650°F with air or helium as working fluids. Preliminary analyses indicate that a direct-contact TES subsystem containing composite carbonate/ceramic-media shapes offers potentially significant reductions in system cost (50% to 70%) and size (30% to 40% decrease in volume) relative to proposed second-generation solar Brayton storage concepts utilizing MgO or Al_2O_3 refractory sensible-heat media.[6]

CONCLUSION

Composite PCM/sensible TES media offer the potential for an economic and direct-contact approach to numerous high temperature industrial/solar as well as medium temperature electrical load-leveling energy recovery and utilization schemes. Appropriate selection of the salt and ceramic materials can result in thermally tailored storage subsystems which can span a very broad range of operating temperature and working fluids. Further work is required, however: TES system economic/performance modeling, evaluation and scale-up before this technology can be practically implemented.

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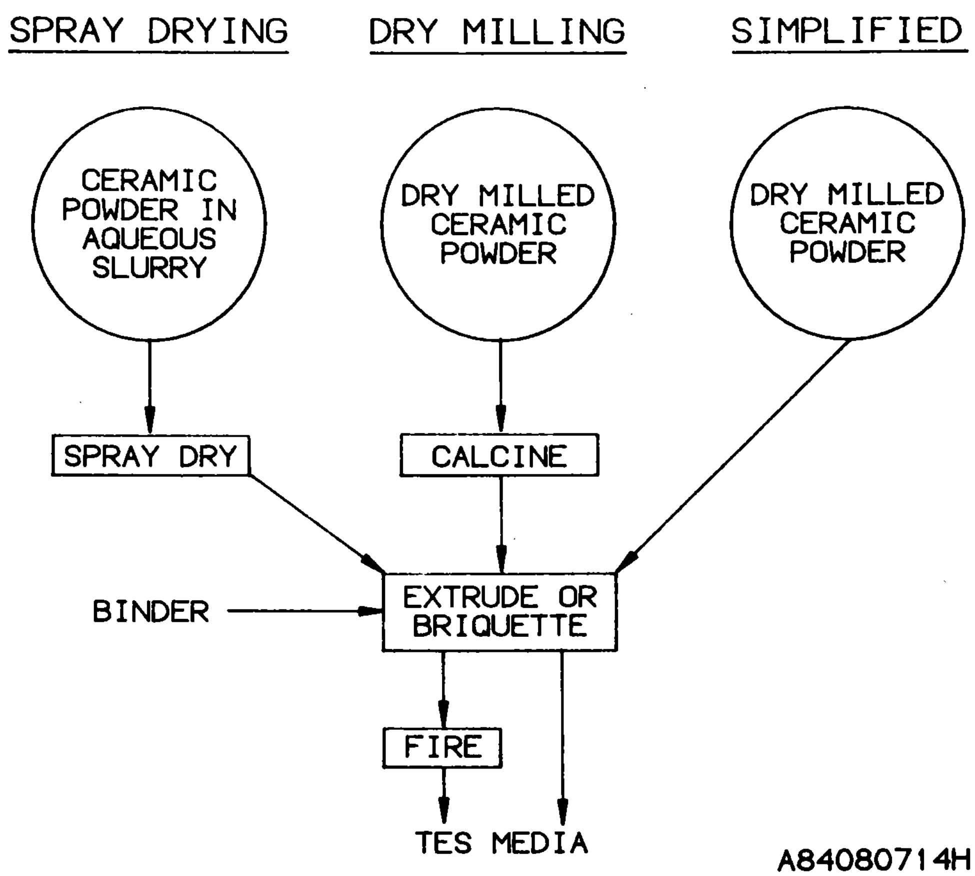

Figure 1. CompPhase™ TES MEDIA PRODUCTION EVOLUTION

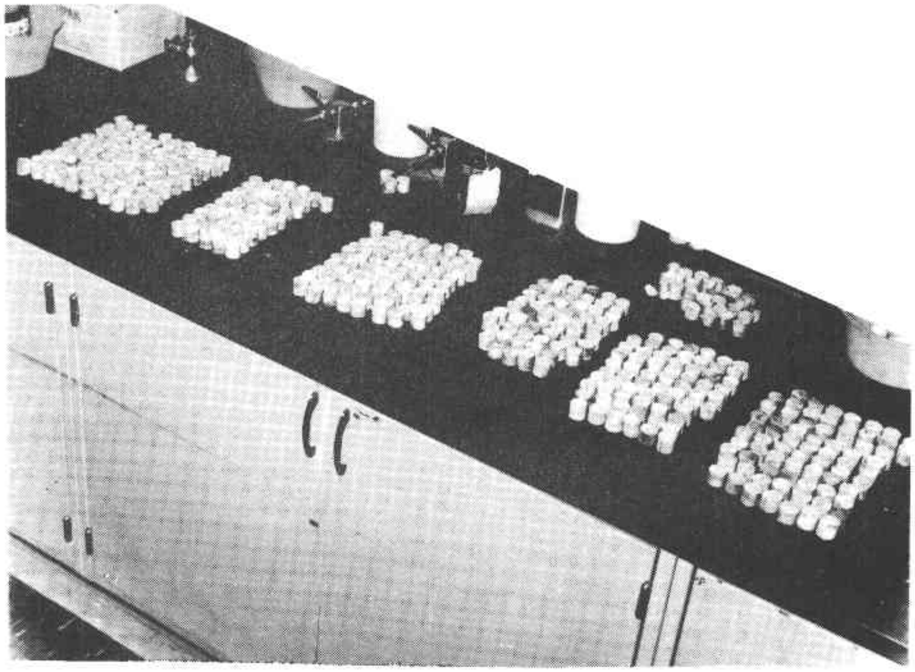

Figure 2. BENCH-SCALE POST-TEST CompPhase™ MEDIA AFTER 6060 HOURS AND 200 THERMAL CYCLES FROM 780° TO 400°C

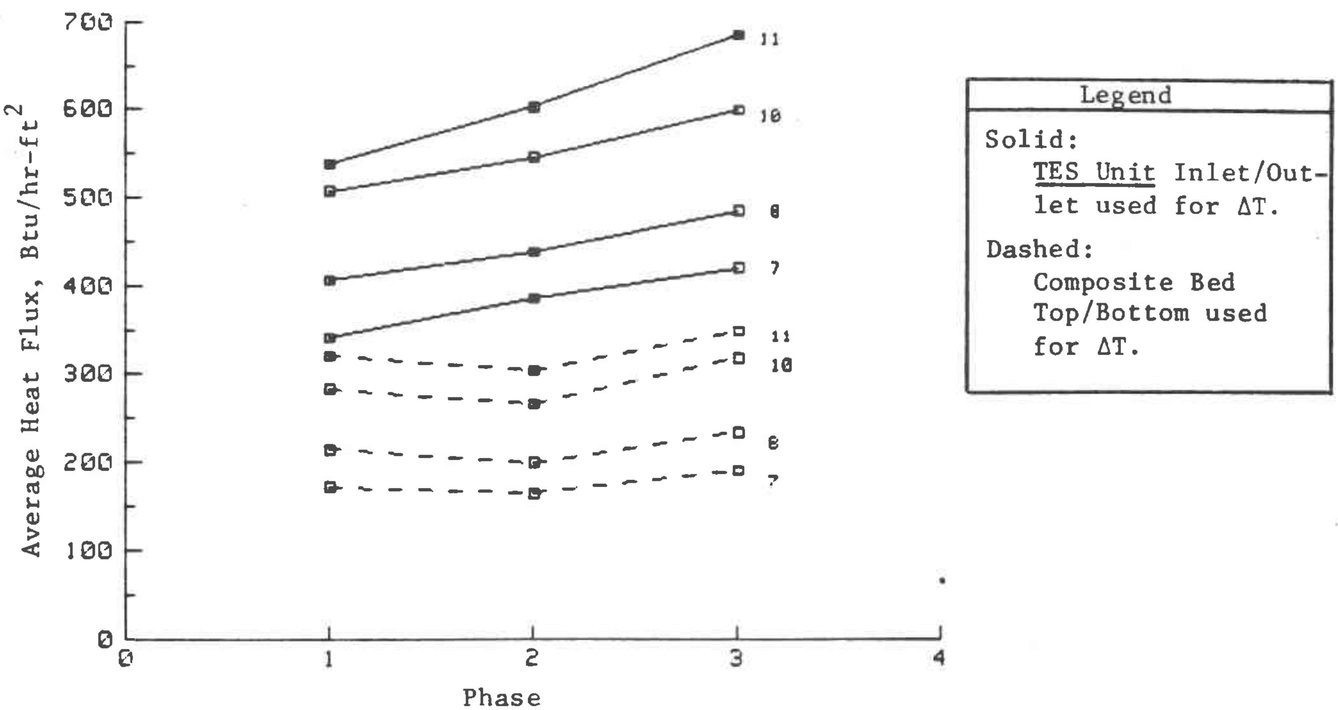

Figure 3. MEAN, EXPERIMENTAL DISCHARGE HEAT FLUXES FOR 51 WT % Na_2CO_3-$BaCO_3$/ 49 WT % MgO FOR PHASE I, II and III

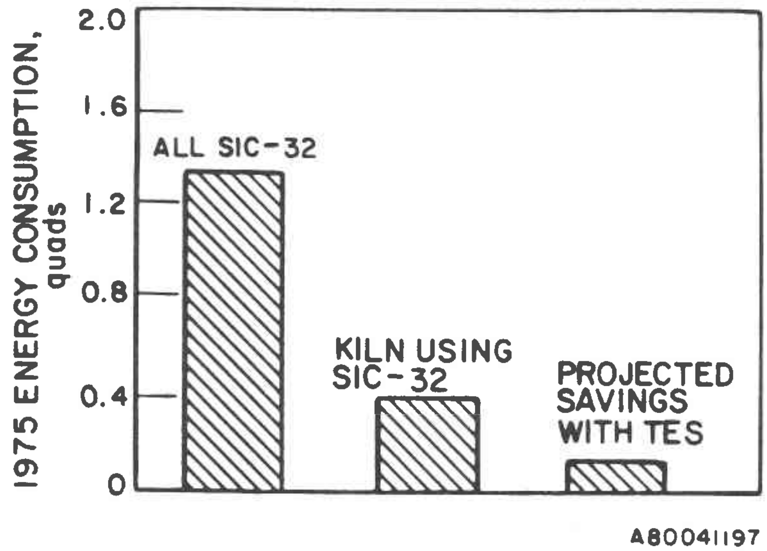

Figure 4. 1981 ENERGY CONSUMPTION IN SIC-32 INDUSTRIES AND PROJECTED SAVINGS WITH TES

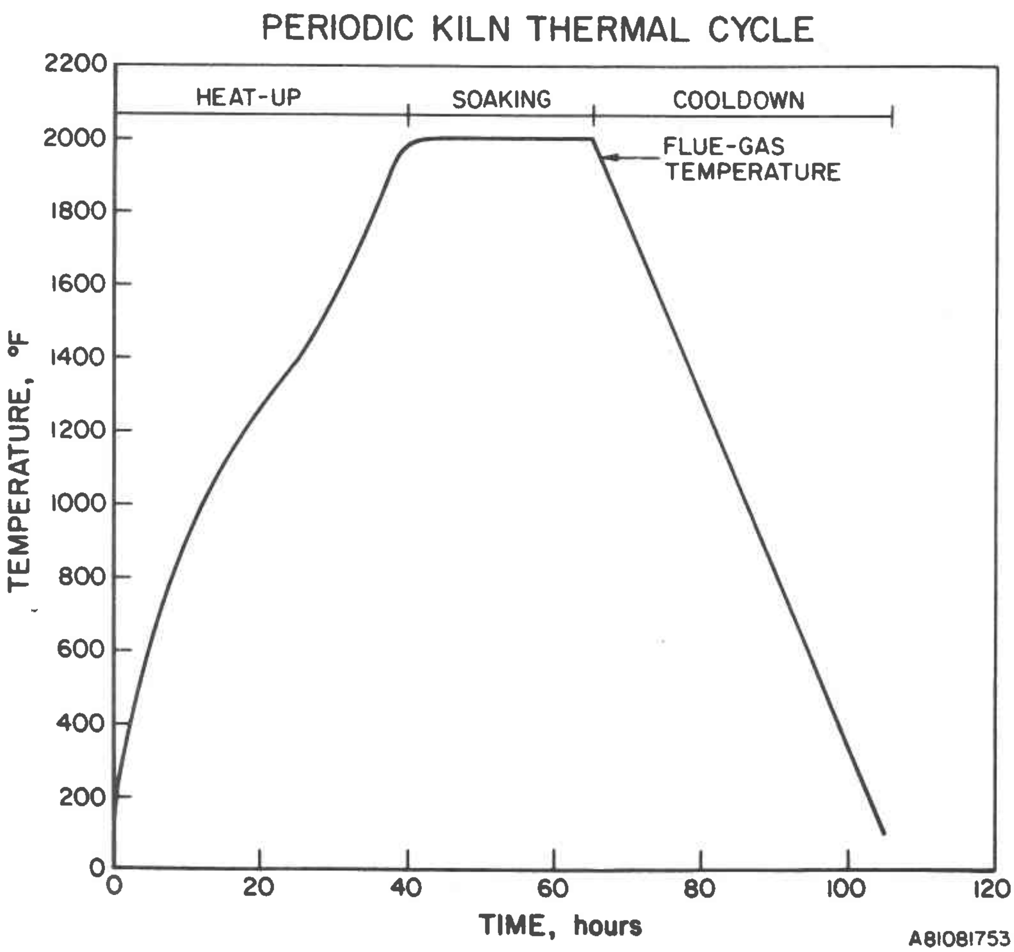

Figure 5. TYPICAL THERMAL CYCLE OF PERIODIC KILN

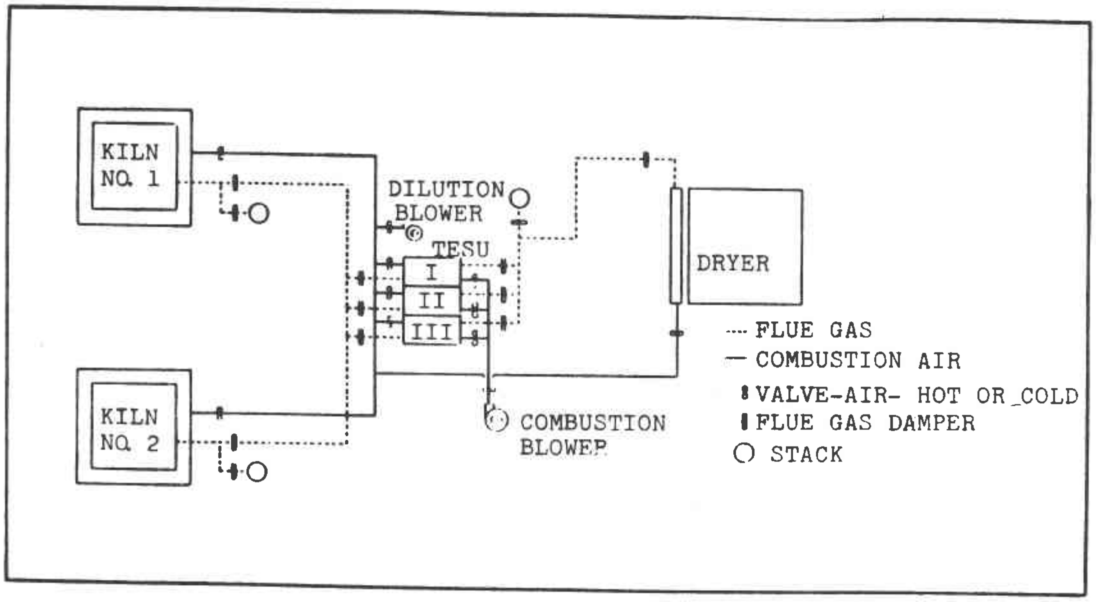

Figure 6. SCHEMATIC OF TES SYSTEM IN PERIODIC KILN APPLICATION