BATCH PREHEAT FOR GLASS AND RELATED FURNACE PROCESSING OPERATIONS

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A. PROJECT GOALS

The objectives that our development work addressed are:

1. Establish through lab tests a salt eutectic with a melting point of about 250 F and a working range of 250 to 1800 F.
2. Establish the most economical material of construction for the screened salt eutectics identified in the first objective.
3. Establish the material of construction for the salt heater liner.

Objectives #2 and #3 were determined through corrosion tests using selected metallurgical samples.

Successful completion of the above-stated goals will be incorporated in a heat recovery design that can be used in high temperature processes and furnaces, typical of which is the glass melting process. The process design incorporates the following unit operations: a vertical batch heater (whereby the batch flows down through tubes in a shell and tube exchanger; a molten salt eutectic is circulated on the shell side); a molten salt heater utilizing furnace flue gas in a radiation type heater (molten salt is circulated in the annular space between the inner and outer shells of the vertical heater, and flue gas passes from the furnace exhaust through the inner shell of the heater); a cantilever type molten salt circulating pump; and a jacketed mixer/conveyor to drive off moisture from the batch prior to feeding the batch to the vertical batch heater. Historically, radiation heaters, when applied to glass or fiberglass furnace recuperation, have experienced failures due to uneven heat flux rates, which increases internal stresses and spot overheating conditions. Low heat transfer coefficients result in requirements for large heat transfer surface areas in gas to gas or gas to air exchangers. Fouling is another factor that results in lower unit availability and reduced performance. These factors are accommodated in this process by the incorporation of several design features. The salt heater will be a vertical double wall radiation design, similar to radiation air heaters used in high temperature heat recovery. The unit utilizes an inner shell that the furnace exhaust gas passes through: this provides essentially a self-cleaning surface. Utilization of radiation air heaters in fiberglass furnaces has demonstrated that the inner shell provides a surface from which molten ash can drain down. The molten salt eutectic will be pumped through the annulus between this inner wall and the outer wall of the unit. The annular space tempering via the molten salt will promote more uniform expansion for the unit, and thereby promote more uniform heat flux rates. Heat transfer would be via radiation mainly, with a minor convective contributor.

B. VARIANCE FROM PROJECT GOALS

The results of tests in this work indicated the following: we were able to synthesize a salt eutectic which has a melting point of 295F, and which is thermally stable up to 1600F under numerous thermal cycling conditions. This deviated from our original goal of 1800F upper temperature capability. However, the salt eutectic formulation achieved here is far superior to any other commercially available, and is a good fit for the heat recovery process we intended it for. The corrosion tests with this salt eutectic demonstrated that alonized stainless steels are resistant to the eutectic at temperatures to 1600F, and will be a suitable material of construction for the batch heater. In later tests, we also identified eutectics with melting points of 235F (test 119) and 285F (test 120). Corrosion tests were performed on sample 120; we did not perform corrosion tests on sample 119, but we expect that the characteristics of this salt will not differ appreciably from sample 101, which was tested. Time did not allow full evaluation of the thermal stability of these salts: we plan on future continued tests to explore these opportunities.

Our corrosion tests with sodium sulfate at high temperatures (1800F) indicated the alonized stainless demonstrated excellent resistance to corrosion and fouling, making this a good material of construction for the eutectic salt heater. The results were dramatic when compared to 316SS under similar conditions.

In the course of the project, we increased the portion of non-Federal funding (that is, funds in-kind contributed by E&ER) via an approved request for a 6-month time extension. This additional effort was directed to testing alternate salt eutectic formulations in an effort to reach higher operating temperature capability. In this work, we found that eutectics using zinc chloride and ferric or aluminum chloride also provided a suitable eutectic composition, while providing

acceptable melting points and upper temperature capabilities. We did not carry these evaluations beyond 1600F.

C. DISCUSSION OF PROJECT RESULTS

1. Salt Eutectic Tests

For the eutectic salt tests, we concentrated our efforts around the chlorides of aluminum, ferric, calcium, sodium, and potassium. The test apparatus consisted of a vertical cylindrical pressure vessel. The top connections to the vessel consisted of a nitrogen supply for padding, a vent, and a sight glass. The sight glass was removed for the higher temperature tests. The bottom connection was used for the thermocouple for temperature monitoring. Heat was supplied via a combination of heat gun and propane burner. For each eutectic prepared, the components were weighed out and placed in a refractory crucible. After thorough mixing, the crucible was placed in the vessel, and the vessel lid was sealed. The vessel was purged with nitrogen, and padded with nitrogen where indicated in the individual test runs. Melt points were then determined by slowly adding heat to bring up the temperature, and observing the crucible contents (through the sight glass) for softening point and melt point. Photos of the test vessel are attached in the appendix.

The prepared mixtures were tested to establish melting points: the results are indicated in the table below. The samples were then screened for melting points near 300F. Three different formulations were selected from this screening for thermal stability testing: samples 101, 105, and 114. For these tests, the sample was subjected to increased temperatures in increments: we started at 900F, and ran each of the three samples through two cycles at this temperature for a 3 hour duration. After each run, the salt sample was examined for visual changes and measured for weight loss. Initial tests on these samples using only a nitrogen blanket (<1 psi) resulted in degradation of all three salts. This is attributed to the volatility of the aluminum chloride. We then increased the nitrogen pad pressure in increments, staying at the 900F temperature. Tests were run with pad pressures of 10, 25, 40, and 60 psig. With each increase, we observed an improvement in the thermal stability of each sample; however, there was no noticeable difference in going from 40 to 60 psig pad pressure. Based on these results, we used a pad pressure of 40 psig for all further tests. The three samples were then thermally cycled in steps up to 1600F: the temperature was increased to 1100F, and again each sample was ran through 2-three hour cycles. The same method was used at levels of 1200, 1400, and 1600F. The samples were examined after each cycle for degradation evaluation. With the 40 psig pad, we found that all three salt eutectics were stable up to 1600F. We did not go over 1600F in these tests due to temperature limitations on our test vessel/apparatus. We therefore used 1600F as our upper temperature limit for the purposes of moving on to corrosion testing.

2. Corrosion Tests with Salt Eutectics

For this series of tests, we selected 304L SS, 316 SS, alonized 304L SS, and alonized 316L SS. We used the eutectic mixtures from tests 101 and 120 (that exhibited stability up to 1600F under a 40 psig nitrogen blanket). For the fist set of tests, the 101 salt was used. The metal sample was inserted in a crucible, along with the salt eutectic mixture. For each run, a 304L SS sample was run along with an alonized 304L SS sample (separate crucibles). Each sample was exposed to ramped-up temperature levels: 1000, 1200, 1400, and 1600F. The sample was exposed to each temperature level for 20-32 hours. Following each temperature exposure, the metal sample was removed and cooled, then examined for visual corrosion/oxidation. Then the respective metal sample was inserted back into its respective salt bath and heated to the next temperature level. The same procedure was used for both salt eutectics being evaluated. For the 101 salt eutectic, at 1400F, some attack was observed on the 304 SS sample. When the sample was held at 1600F, there was fouling and loss of metal from oxidation corrosion/scaling. This is shown in Photo MS-1. The alonized sample showed no deterioration at 1400F, and at 1600F showed some minor fouling (MS-2). The sample was cleaned and inspected (MS-3): the metal was discolored, but there was no evidence of oxidation scale or corrosion products. Thus, the alonized stainless is an acceptable metal for this salt eutectic system.

Using the 120 salt eutectic, the same test procedure was used as outlined above. MS-4 shows the 304L SS sample after being subjected to 1200F. There was some surface oxidation on the specimen, but of a minor nature. At higher temperatures, there was increased oxidation, indicating the 304L is not acceptable at 1600F, our target temperature. The alonized 304L SS sample was tested in the same manner: the results indicated this is an acceptable metal for use in this eutectic system also. MS-5 shows the alonized 304L after exposure at the 1500F level. There was some discoloration of the metal, but no indications of corrosion products or oxidation/scaling.

We conclude from this series of corrosion tests that the alonized 304L/316L stainless steels are acceptable materials of construction for the batch heater.

3. Corrosion Tests with High Temperature Sulfate Exposure

In this series of tests, the metallurgical samples were tested for resistance to high concentrations of sodium sulfate at high temperatures. These tests followed the same procedure as the corrosion tests using salt eutectics. For these tests, temperature levels used were 1300, 1500, 1700, and 1900F. The results indicate that 304SS is acceptable at 1300F, but not higher; 316SS is acceptable at 1500F, but not higher. Oxidation and corrosion fouling increased rapidly above the respective temperature for these stainless steels. Photos S-1 and S-2 show the almost complete destruction of the 316SS when ramped up to 1900F over the indicated temperature levels. In contrast, the alonized 316L sample was in excellent condition when subjected to the same conditions. Of particular impact is the minimal fouling on the alonized sample (see Photos S-3, S-4, and S-5). This illustrates that the surface of a radiation heater lined with this material can indeed remain virtually unfouled in service, as the molten sulfate can run down the exchanger surface and back into the furnace.

FUTURE TESTING

E&ER plans to continue a test program beyond the work contained in this contract. Our plan includes:

-Thermal stability tests on $ZnCl_2$ and $FeCl_3/AlCl_3$ salt eutectics.

-Thermal stability and corrosion tests up to 1800F with 101, 119, 120, and 121 salts.

-Bench tests with a batch heater using the optimum molten salt and metallurgy. As part of this test, we will have Alon Surface Technologies evaluate the heater tube which will be used in this model. In this work, we propose to fabricate a bench scale batch heater to test the new salt and metallurgy. We will use prepared batch mixtures as used in float and silicate glasses. This will be important to determine whether plugging problems occur due to batch retained/chemically bonded moisture or pre-reaction/softening. We will use a double-shell exchanger, with the eutectic salt in the annulus and the batch flowing down through the inner tube. For this testing, we will use an 8 ft long vertical heater, utilizing a 2" inner tube (batch will flow down inside this tube), and a 3" outer tube. An impedance electric heater will be used on the exterior of the 3" outer tube to maintain the salt at 1600F. Impedance heaters are available which can maintain pipe temperatures up to 1800F. A connection will be provided at the top of the annular space for nitrogen padding and venting. There will be a small hopper at the top of the heating section for batch holdup volume, and there will be a small discharge hopper with a knife gate valve to allow control of batch flow. We will operate the heater at different batch plug-flow velocities. A plot will be logged to show batch exit temperature versus velocity. The batch velocity will be optimized to attain the highest approach temperature. The batch will also be tested at low plug flow velocity (i.e.- 0 to 5 feet per minute) to evaluate plugging potential. The zero flow condition (when a batch charger feed is shut down due to other furnace problems) is expected to be the most problematic. In this case, localized heating of the batch will result in batch temperatures approaching 1600F. This will cause the batch to pre-react and soften. To address this situation, we will perform tests to determine whether maintaining batch movement will prevent buildup or bridging problems. If bridging inside the tube is encountered, we will use hot air injection near the point of plugging to maintain batch movement. We have successfully used this technique in prior test work.

In our prior batch heater field tests where HiTech salt was used, the heater only operated at about 1050F salt temperature, and therefore pre-reaction and softening were not a concern. The proposed testing here will establish when and what temperature levels affect flowability of the batch, and what design features can be incorporated to eliminate these problems in order to attain the highest feasible batch temperature.

The viability of the proposed process has been demonstrated in previous pilot testing. The process will be ready for plant field-testing upon completion of the bench scale batch heater tests. Success with past heater designs, along

with the successful development of a new salt eutectic and identification of system metallurgy, have provided strong impetus to continue the preheat process development.
Research/development on batch heating technology has slowed to the point where there is no commercially available technology, except for glass cullet preheater equipment. However, there is still a strong interest in batch preheat within the industry, and there are recent patents to support this interest (e.g.- Corning Glass, Edmeston AB- Sweden, Gas Research Institute). Also, BOC Gases and Praxair Technology are pursuing process routes for batch heating- these processes have not been tested on a pilot scale yet. There is interest in batch preheat technology by the oxygen producers: heat recovery from the furnace would improve the economics of oxy-fuel combustion compared to conventional air-fuel systems. Thus, the market potential is still wide open for the introduction of a technology that is economical and easily retrofitted into existing facilities.

Our goal is to continue a program to achieve commercialization. It is the intent of E & ER to license or sell this technology. Based on completion of the above-mentioned future tests, we foresee a Category 2 proposal in the next 12-18 months. This proposal would encompass a scaled-up pilot system that would provide operating data that can be used in full-scale system designs. This design data will also be used to more accurately determine system capital and operating costs.

Weight Per Cent of Components

Test # >>>	101	102	103	104	105	106	107	108	109
NaCl	30	30	20				15	10	10
AlCl3	60	65	70	60	60	50	60	60	60
FeCl3	10	5	10	10	10	10	5		
CaCl2				30		20	20		30
KCl					30	20		30	
Melt Point, F	299	295	302	320	300	330	325	335	340
N2 Pad, psi	40	45	45	40	45	45	40	40	40

Weight Per Cent of Components

Test # >>>	110	111	112	113	114	115	116	117	118
NaCl	30	30	10	10	31	10			
AlCl3	60	60	30	20	69	80	60	60	40
FeCl3			10	10					
CaCl2	10			10			40		
KCl		10	50	50		10		40	60
Melt Point, F	310	305	325	340	307	320	360	315	325
N2 Pad, psi	45	45	40	40	40	45	45	45	45

Weight Per Cent of Components

Test # >>>	119	120	121						
NaCl	23								
AlCl3	77		59						
FeCl3		64							
CaCl2									
KCl									
ZnCl2		36	41						
Melt Point, F	235	285	300						
N2 Pad, psi	45	10	40						

Attachment A

Completed Milestone Table

Task	Milestone/Task Title	Original Planned Completion Date	Revised Planned Completion Date	Actual Completion Date	Responsible Organization	Original Projected Cost (Fed/ Non-Fed)	Revised Projected Cost (Fed/ Non-Fed)
1	Bench scale testing to establish molten salt eutectic	July 1, 2001	March 1, 2002	March 10, 2002	E&ER Engineer	$20,000/ $5,000	$20,000/ $14,000
2	Bench scale corrosion testing to determine salt system metallurgy	August 1, 2001	March 31, 2002	May 15, 2002	E&ER Test Engineer	$8,000/ $3,354	$8,000/ $4,074
3	Bench scale testing to determine salt heater liner metallurgy	October 1, 2001	September 15, 2001	September 15, 2001	E&ER Test Engineer	$6,000/ $0	$6,000/ $0
4	Attend annual project review	TBD	TBD	--	E&ER Principal Investigator	Included in Task 5	Included in Task 5
5	Project management and reporting	October 1, 2001	May 15, 2002	May 15, 2002	E&ER Principal Investigator	$6,000/ $3,000	$6,000/ $3,000
6	Final report	January 1, 2002	June 1, 2002	August 20, 2002	E&ER Principal Investigator	Included in Task 5	Included in Task 5
Final Mile-stone						$40,000/ $11,354	$40,000/ $21,074

Attachment B

Final Gantt Chart

Milestone/ Task Number	Milestone/Task Title	2nd Quarter 2001	3rd Quarter 2001	4th Quarter 2001	1st Quarter 2002	2nd Qua 2002
Milestone 1	Bench scale testing to establish molten salt eutectic	X X X	X X X		X X X	
Milestone 2	Bench scale corrosion testing to determine salt system metallurgy		X X X	X X X	X X X	X X
Milestone 3	Bench scale testing to determine salt heater liner metallurgy	X X X	X X X			
Milestone 4	Attend annual project review			TBD		
Milestone 5	Project management and reporting		X X X	X X X	X X X	X X
Milestone 6	Final report					X

Attachment C

Energy, Environmental, and Economic Savings for I&I

The installed unit for the *I&I project* technology is _____150 TPD Glass Furnace_____.

The installed unit for the *comparable competing* technology as presented in the original proposal is

___150 TPD Glass Furnace_____.

Energy Savings

Provide the energy savings for the project technology versus the comparable competing technology.

The *projected* energy consumption for the *project* unit in Btu/yr/unit was (at the beginning of the project)

4.5 MM BTU/Ton Glass.

The energy consumption for the *I&I project* unit in Btu/yr/unit is 4.5 MM BTU/Ton Glass (estimated), or 235,000 MM BTU/year/unit.

Provide assumptions and references for the derivation of your values. *(Refer to Attachment H for energy conversion factors*) The pilot testing by this inventor demonstrated a 20 % reduction in energy requirements per ton of glass, while increasing the melt rate 15% (on a tons glass per square foot of hearth basis): this was achieved using HiTech salt at 1000F operating temperature, yielding a batch preheat temperature of 750F. This was consistent with literature references relating to potential energy savings with batch preheat. The present proposed work seeks to extend this prior testing, whereby batch preheat levels can be increased and achieve some level of pre-reaction of the batch prior to injection into the furnace. It is projected from earlier work that 30% energy reduction can be achieved with 1200F batch feed temperature. The previous work demonstrated successful heat exchanger designs for this application. Literature (cited references in Bibliography) indicates that batch preheat can yield savings of 20% to 30% in fuel usage. This inventor validated these estimates in field tests. Studies by others

indicate potential fuel reductions of 8 to 30 x 10E6 million BTU/yr for utilization of batch preheat, with additional savings if this technology can be used in related industries (i.e.- fiberglass, mineral wool).

The energy consumption for the *comparable competing* unit in Btu/yr/unit is 6.5 MM BTU/Ton Glass, or 340,000 MM BTU/year/unit.

This is an industry average, and is well documented (references 1 and 5 in bibliography).

Environmental Savings

Provide the environmental savings for the project technology versus the comparable competing technology.

The *projected* wastes other than power generation emissions for the *project* technology in tons/yr/unit using the *I&I project* unit described above (at the beginning of the project) were:

Waste 1 29,400 CO2

Waste 2 66 NOx

Waste 3 440 Particulates

Identify wastes other than power generation emissions for the *I&I project* technology in tons/yr/unit using the *project* unit described above:

Waste 1 29,400 CO2

Waste 2 66 NOx

Waste 3 440 Particulates

Identify wastes other than power generation emissions for the *comparable competing* technology in tons/yr/unit using the

comparable competing technology unit described above:

Waste 1 _____42,000 CO2_____

Waste 2 _____95 NOx_____

Waste 3 _____630 Particulates___

Provide assumptions to allow reviewers to understand the derivation of the stated values.

Along with the energy reduction there would be a reduction in air emissions, particularly submicron particulates, CO2, and NOx in direct correlation to the energy reduction. Field-testing will be necessary to more accurately determine emissions reductions. The above estimates are based on EPA emission factors for natural gas combustion, and then using the 30% reduction based on the 30% fuel usage reduction.

Economic Savings

Provide the economic savings for the project technology versus the comparable competing technology.

The *projected* unit cost for the *I&I project* technology (at the beginning of the project) was

_____

Define the unit cost for the *I&I project* technology _____$705,000/year_____

Define the unit cost for the *comparable competing* technology _____$1,000,000/year___

Provide assumptions to allow the reviewers to understand the derivation of the stated values.

The above costs are based on the annual fuel usage at $3.00/MM BTU (natural gas). These are conservative figures, in that

many glass plants utilize #6 oil and/or electric melters or electric boosting at a significantly higher fuel cost. Also, the capital cost for a new plant will be lower for the I&I project case: there will be substantially less refractory due to the elimination of checker chambers (which are used to preheat combustion air in the competing technologies). The I&I project case will utilize the batch heater followed by a metallic recuperator in place of conventional checkers. This also results in less solid waste generation: checker chambers must be rebuilt on a routine basis, resulting in waste refractory brick generation.

Attachment D

Fuel /Energy Source Btu Conversion

Fuel Source	Btu/Barrel	Btu/Gallon	Btu/Pound	Btu/ft^3
Crude Oil	6×10^6	142×10^3	18.6×10^3	1×10^6
Fuel Oil – 6	6.2×10^6	150×10^3	17.8×10^3	1.1×10^6
Fuel Oil – 2	6×10^6	140×10^3	18.6×10^3	1×10^6
Gasoline	5.2×10^6	126×10^3	18.9×10^3	940×10^3
Propane – L	3.8×10^6	92×10^3	19.9×10^3	690×10^3
Wood	-------	-------	6.5×10^3	148×10^3
Natural Gas	87×10^6	2×10^3	21×10^3	1×10^3
Methane	87×10^6	2×10^3	21×10^3	1×10^3
Methanol	2.9×10^6	69×10^3	9.6×10^3	517×10^3
Ethane	-------	-------	20×10^3	1.8×10^3
Ethanol	3.7×10^6	87×10^3	12×10^3	652×10^3
Hydrogen	-------	-------	51×10^3	270
CO	-------	-------	4.3×10^3	316
Coal - Bit.	-------	-------	12.6×10^3	800×10^3
Coal - Lig.	-------	-------	8.6×10^3	541×10^3
Coal - Ant.	-------	-------	12.6×10^3	800×10^3
Carbon	-------	-------	14.6×10^3	1.9×10^6
Ethylene	-------	-------	20×10^3	1,477

Electrical Generation (32.4% efficient Power Plant) – 10,500 Btu/kWh

Attachment E

Commercialization Table
(I&I Category 2 Projects Only)

Category	U. S. Market				
	Project Completion Year	**5 Years after Completion**	**10 Years after Completion**	**15 Years after Completion**	**20 Years after Completion**
(A) Total Number of Units in U.S. Market (Addressable Market)	**NA**				
(B) Total Number Installed Units Using Your Technology (Capturable Market)	**NA**				
(C) Market Penetration = B/A x 100%	**NA**				

?? **Your technology** - Total number of units employing the technology developed with the I&I grant. This number includes, but is not limited by the number of units that the industrial partner will sell or operate.

?? **Addressable Market** is that fraction of the entire market to which your technology is truly applicable. Remember to project the number of installed units by first considering limiting factors related to technology and market fit. For instance, the proposed technology may only fit a certain size range of equipment, i.e., a proposed glass furnace burner technology can only be constructed is sizes smaller than 5 MMBtu/hr, or the proposed burner can only be applied to recuperated furnaces, not regenerative furnaces.

?? **Capturable Market** is that fraction of the Addressable Market willing to accept your new technology. Remember that the rate at which industrial technologies capture the market depends on technology characteristics (new vs. retrofit), industry characteristics (industry growth, competition), and external factors (government regulations and trade restrictions). Consider these limiting factors related to rates of market acceptance before projecting the number of installed units in the Capturable Market.

Attachment F

Final Cost Sharing

#	Company Name	Company Type*	In-Kind Contribution	Cash Contribution	Total
1	**Energy & Environmental Resources**	**Small Business**	**$19,074**		**$19,074**
2					
3					
4					
5					
	DOE			**$40,000**	**$40,000**
	Total			**$40,000**	**$59,074**

Only Include Cost-sharing Partners

***** small business, business, non-profit, university, state agency, or utility

Attachment G

Partners and Contractors

#	Company Contact	Address	City	ST	Zip	Phone / Fax / e:mail
1	**None**					
2						
3						
4						
5						

List all companies involved in the project (equipment vendors, consultants, subcontractors, customers etc. and provide a brief narrative discussing the role of each partner.)

1)

2)

3)

4)

5)

Photos Cross -Reference List

Photo #	File #
MS-1	101_304-1.jpg
MS-2	101_alon-1.jpg
MS-3	101_alon-cleaned.jpg
MS-4	120_304.jpg
MS-5	120_alon.jpg
S-1	316L_#9a.jpg
S-2	316L-aged.jpg
S-3	alon316L_#15a.jpg
S-4	alon316L_#15b.jpg
S-5	alon316L_cleaned.jpg

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2. Glass Batch Preheater -Thermo Electron Corp.
NTIS PB84-101427 Prepared for Gas Research Institute, May 1983

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Corning Glass Works NTIS PB81-175929
Prepared for Industrial Environmental Research Lab- Cincinnati, Ohio
March 1981

4. Ditto above: Phase IIA, Process Design Manual
EPA/600/S2-85/073 August 1985

5. Market Impact of Glass Batch Preheaters -Working Paper
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