ENERGY RECOVERY SYSTEMS IN SOLID OXIDE FUEL CELL SYSTEMS

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ABSTRACT

Solid oxide fuel cell is an electrochemical energy conversion device, which directly converts chemical energy of a hydrocarbon into electrical energy and heat energy. These devices operate isothermally at high temperatures(800–1000 °C). In order to enhance total energy efficiency of these type of devices, heat from out-going gas streams should be recovered and utilize to heat incoming gas streams. For further energy utilization, any unburned gas can be burned using catalytic converters or burners, and additional heat supply can be recovered from the streams using heat recovery heat exchangers and up to 95 % total energy recovery from the chemical fuel in the form of heat and electricity.

INTRODUCTION: GENERAL PRINCIPLES OF FUEL CELLS

Solid Oxide fuel cell is all in solid electrical power conversion systems. The basic building blocks of the solid oxide fuel cells are yttrium-stabilized zirconia electrolyte layer. Strontium doped lanthanum manganite and nickel zirconia cermet is used as anode and cathode materials.

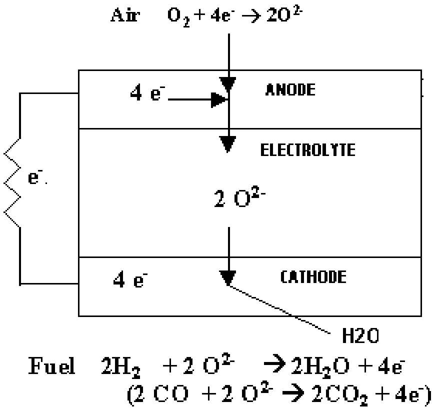


Figure 1 General operation principles of solid oxide fuel cell

General operation principles of the solid oxide fuel cell are shown in Figure 1. Yttrium-stabilized zirconia is sufficiently ionically conducting above 800°C. At anode H_2 or CO reacts with oxide ions transported through the electrolyte to form water. This is accompanied by the release of electrons to the external circuit. Electrons from external circuit react with oxygen at the cathode and produce oxide ions. The overall process is the reaction of oxygen with hydrogen and/or carbon monoxide to produce water and carbon dioxide Ionic conductivity of the electrolyte usually increases with temperature and decrease with the plate thickness. Plate thickness used is about 50 microns to 150 microns. This thickness dictates cell temperature of 800 to 1000 °C.

Some means of transferring air and fuel stream to the cell, and a mechanism of transferring electrical current from the cell is also needed. In simple plane solid oxide fuel cells interconnects plates, as given in Figure 2, are used. When several interconnect plates are used in serial, it creates a fuel cell stack. Figure 3 shows a plane solid oxide fuel cell stack. This stack consists of 50 layers. Every layer contains eight of 100 mm by 100 mm size fuel cell, total of 400 cells delivering 5 kW of power. We can consider this structure as a stack of 8 parallel 50 serially connected batteries. Each fuel cell delivers about 1 to 1.2 volt at open circuit depends on water content and actual fuel mixture. Under the electrical load, the cell voltage drops to 0.7–0.9 V. The difference is due to the electrical resistance inside of cells and current passing through interconnects plates. This resistance converts to heat energy and the main source of the fuel cell system irreversibility.

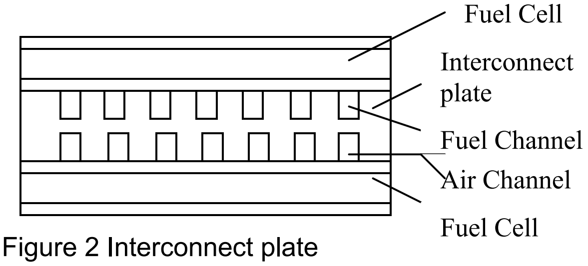


Figure 2 Interconnect plate

High temperature isothermal operation conditions and stack heat generation suggests utilization of heat exchangers between incoming and exhaust streams for air and fuel sides. Air and fuel streams are also needed to pump through the system and finally exhaust gases should be safely exhausted to the atmosphere. All this kind of requirements creates a need for a fuel cell system around the fuel cell.

FUEL CELL SYSTEMS

A natural gas fuelled solid oxide fuel cell system flow diagram is shown in Figure 4. As seen from the flow diagram, two main gas streams exist in the flow diagram. The first stream is the air stream. The air stream enters to the system through a blower. Then the air goes through a process air heat exchanger. In normal operation conditions, air stream should be heated up about 700°C at the exit of the heat exchanger. At the exit, an electrical heater is located. The main duty of this heater is to supply starting energy and temperatures for the heater. Once operating conditions of the fuel cell is reached, electrical heater is turned off, and fuel cell is used as the main heat source. Gas stream exit the fuel cell at 930°C and input the process air heater as hot gas stream. In this stage, some of the oxygen in the original air is already spent in the fuel cell. Therefore this gas stream is called depleted air stream. When depleted air passed through process air heat exchanger, it is cooled down to about 200°C. Depleted air is then sent to the catalytic reactor.

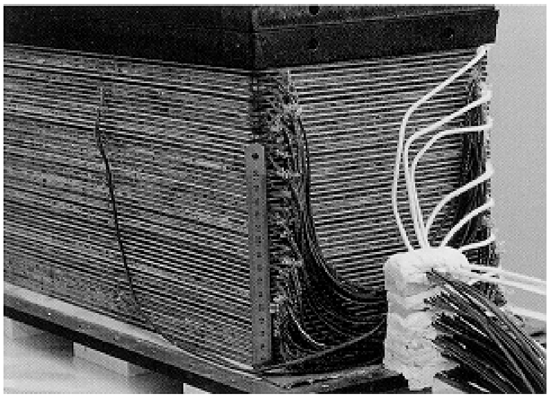


Figure 3 The stack of fuel cells and interconnect plates

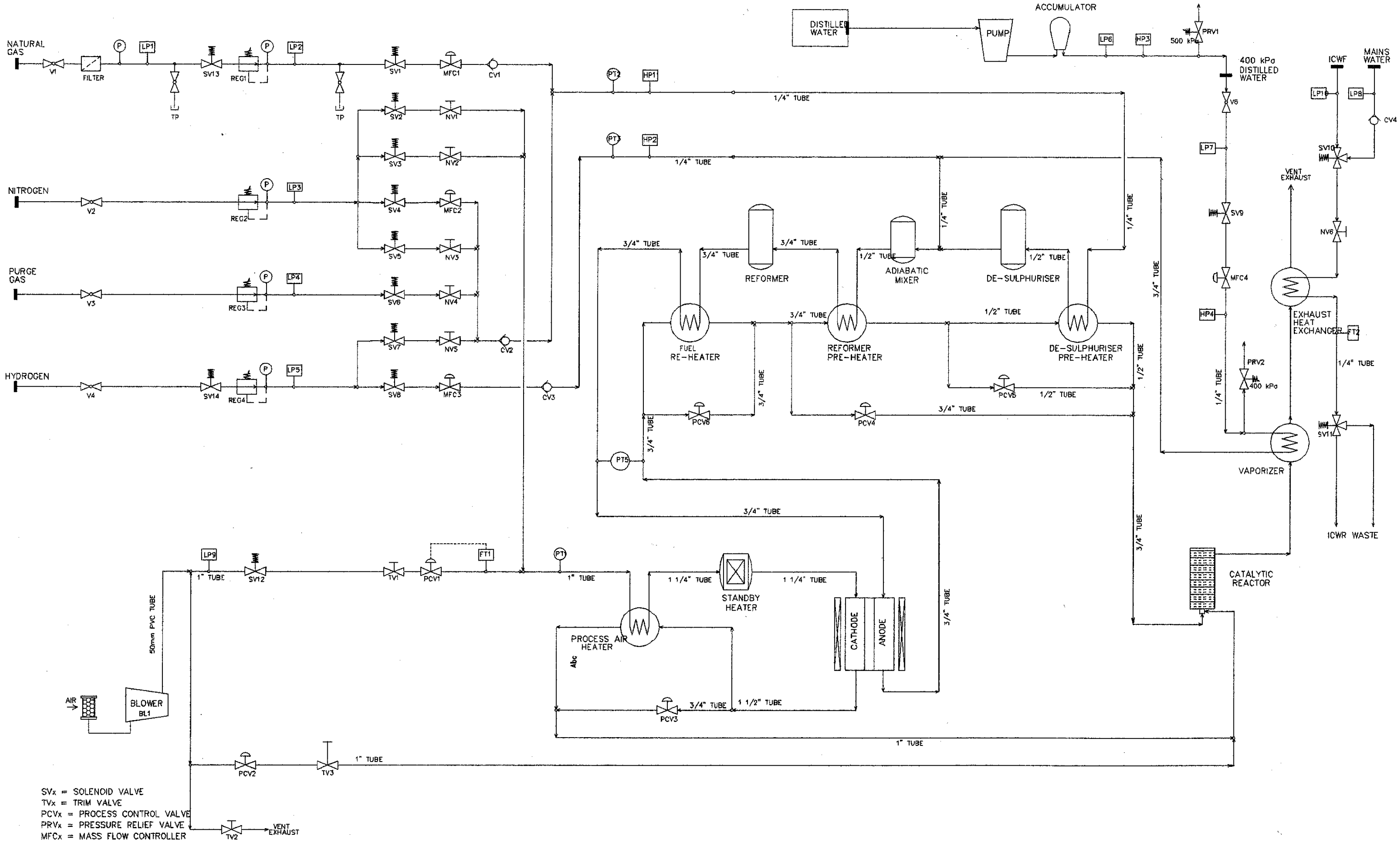
Natural gas stream with main gas pipe-line pressure of 40 kPa is used; therefore no additional fan or compressor is needed in fuel stream. Natural gas is first enters de-sulfuriser preheater. In this heat exchanger, it is heated to 300°C. It is then entered to desulphuriser. Sulphur and sulphur compounds are chemically bonded to de-sulphurization catalysts inside of the de-sulphuriser. Desulphurised natural gas entered to an adiabatic mixer and mixed up with steam and entered to catalytic reformer. Natural gas mix is heated up to 500°C, in another heat exchanger, Then it is entered an adiabatic reformer. In this reformer, high carbon number hydrocarbons are broken to methane and hydrogen by water shift reaction on nickel based catalyst surfaces. This process is called adiabatic fuel reforming. At the exit of the adiabatic reformer, mixture is cooled down to about 300°C because of the energy taken by reforming process. This mixture is went through another heat exchanger and heated to about 700°C before going to the solid oxide fuel cell stack. In the first stage of the stack, the rest of the methane is also converted to CO and hydrogen by internal reforming process. Internal reforming process is similar to reforming process, but instead of catalysts electrochemical reactions forced the mixture into equilibrium condition. Converted fuel then undergoes an electrochemical cell reaction and creates heat and electricity. 85% of the fuel is converted into the cell through electrochemical reaction. The rest of the gas together with combustion gases comes out of the fuel cell at 930°C. This stream, called depleted fuel stream, goes through the three stages of heat exchangers and heating up incoming streams. Relatively cooled depleted fuel finally enters to catalytic reactor and reacts with depleted air and additional fresh air. Catalytic reactor is made of platinum embedded metal surface.

Small quantities of hydrocarbons can react on these surfaces. Reheated final combustion gases pass through a water evaporator to supply system steam requirements for reforming process. A further heat exchanger is taken any heat left in the exhaust stream and cooled exhaust is released to the atmosphere. As another stream water is purified then pressurized through a pump and send to the water evaporator.

After this general information about fuel cells, we investigate energy recovery systems used in the solid oxide fuel cell systems.

REQUIREMENTS FOR AIR AND FUEL STREAM HEAT EXCHANGERS

Because of the high temperature operations and the process described above air and fuel stream



SVx = SOLENOID VALVE
TVx = TRIM VALVE
PCVx = PROCESS CONTROL VALVE
PRVx = PRESSURE RELIEF VALVE
MFCx = MASS FLOW CONTROLLER
NVx = FLOW REGULATING NEEDLE VALVE
FTx = FLOW TRANSDUCER
L.Px = LOW PRESSURE SWITCH
H.Px = HIGH PRESSURE SWITCH
CVx = CHECK VALVE
REGx = PRESSURE REGULATOR
PTx = PRESSURE TRANSDUCER

Figure 4 A Natural Gas fuelled,Solid oxide fuel cell System

Heat recovery exchangers requirethe following:

- Exchangers should be compact enough to meet for high temperature operation and insulation conditions.
- Total pressure drop of the system should not exceed 3 kPa in the airside and should also be in similar order of magnitude in order to match pressure balance in the both side of the fuel cell pressure.
- Heat exchangers should have at least 10000 hour of operation time. Therefore high corrosion resistance should be existed.
- Air stream heat exchanger should have a temperature difference of about 700°C. Therefore they should be counter flow heat exchangers.
- Fuel heat exchangers should be completely leak free during the total operation time.
- Both air and fuel streams should be controllable by bypass valves. These valves should be operable in high temperature conditions.
- Evaporation of chromium from the exchanger surface end emigration of chromium gases to the fuel cell surfaces should be avoided.

After some investigation, it was found out that no commercial product could match to these conditions. So a development program is started.

DEVELOPMENT OF AIR AND FUEL HEAT EXCHANGERS

High-temperature differences require the counter flow heat exchangers. The compact size requirement suggests plate type heat exchangers. Chevron type plate heat exchangers are considered, but it is found that their pressure drop was too high for out gas-to-gas applications. Special flat plate and dimpled plate heat exchangers with relatively low-pressure drop are considered as the basic design selection. In these heat exchangers, heat is transferred through relatively thin plates (0.35 mm). 1.5 mm thick interconnect plate is used to divert flow to actual rectangular channels. They also function as metal gaskets, as shown im Figure 5.

Figure 6 shows a flat plate fuel heat exchanger thin plate, interconnect plate and the top plate. Figure 7 shows a dimpled plate heat exchanger thin plate configuration. As heat exchanger material, first Sandvick 253MA stainless steel is used. This steel has extraordinarily high corrosion resistance, but in actual operations it is found that thermal cycle corrosion resistance was not as high. Material is flaked off from the surface after each heating and cooling cycle. Its thermal expansion coefficient was also very high. Later, 253MA is replaced with 800H stainless steel, which has relatively high corrosion and thermal cycle corrosion resistance. It is also structurally strong at high operating temperatures.

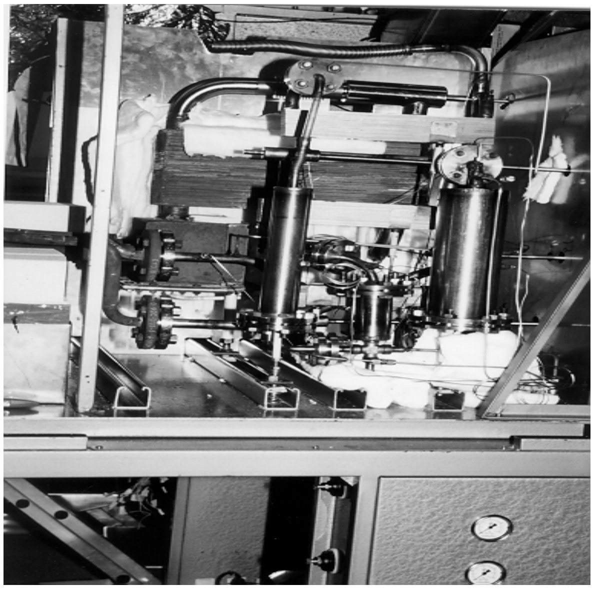
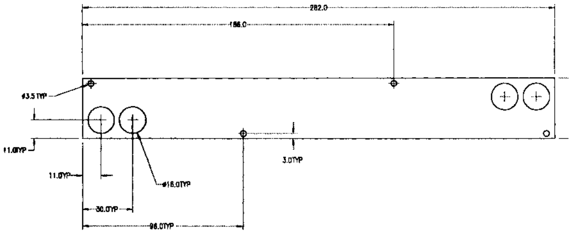


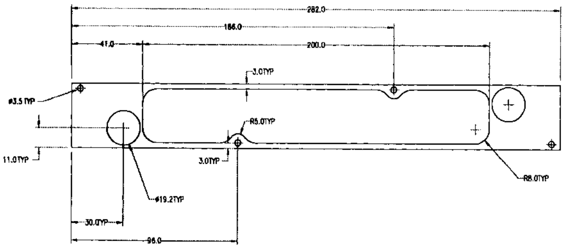
Figure 5 1.5 kW Natural gas fuel, solid oxide fuel cell system.

Thin plates; interconnect plates and top and bottom plates were connected together using a high temperature brazing process. A nickel based brazing powder is converted to a paste or a gasket using an organic binder. Paste is applied to the surfaces required to braze together. Then all the plates come together to form the heat exchanger. Formed heat exchanger was heated in high vacuum furnace at 1300°C where brazing alloy is melted and bind the surfaces together. All the impurities in the alloy including organic paste binder were evaporated and left a pure nickel-bonding layer between the plates. Heat exchangers were pressure tested. Where of any leakage discovered, another brazed paste fixing layer was applied from the outside surface. Due to impurities like boron in the brazing alloy, melting temperatures of nickel were lower in the paste compare to the previously applied nickel binding. This allowed reapplication of the brazing material to fix any leakage left in the first application.

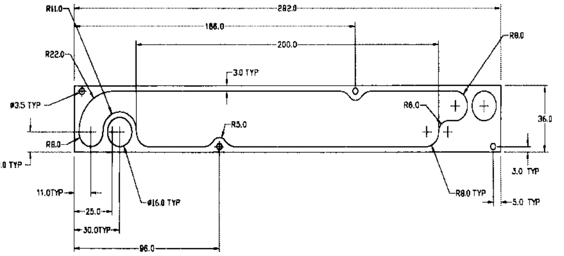
As the last process, metal surfaces covered with a layer of alumina (aluminium oxide) for high temperature corrosion resistance. It was found that chromium oxides are creating an electrical insulating layer for fuel cell surfaces. In order to prevent this effect chromium propagation from anywhere in the system should be avoided. A process called colorizing was applied to create this necessary protective layer. Heat exchangers were cleaned by using acid bath then surfaces are wetted with the alumina solution in the liquid bath. Any excess material was forced to flow out of heat exchanger channels. Heat exchanger body was heated to 1300°C in an inert gas (nitrogen) furnace. After this process, the surface was covered with an aluminium oxide layer. This layer is not only protective against corrosion and chrome propagation, but also self-healing. If surface is stretched for some reason, aluminium propagated from internal layer to the surface and re-coated the surface.



a) thin plate



b) top plate



c) interconnect plate

Figure 6 kW Natural gas fuel heat exchanger plates

CALCULATIONS OF AIR AND FUEL HEAT EXCHANGERS

For the calculation and simulation of heat exchangers, finite different analysis with object-oriented programming is used. All programs are developed initially in **C++** language and later translated to **Java** language.

The following set of classes are prepared to achieve an accurate simulations of the heat exchanger systems:

Atom: properties of individual atoms

Gas : Thermo physical properties of ideal gases (Enthalpy is the function of temperature, entropy function of temperature and pressure) including viscosity, Prandtl number and Thermal conductivity

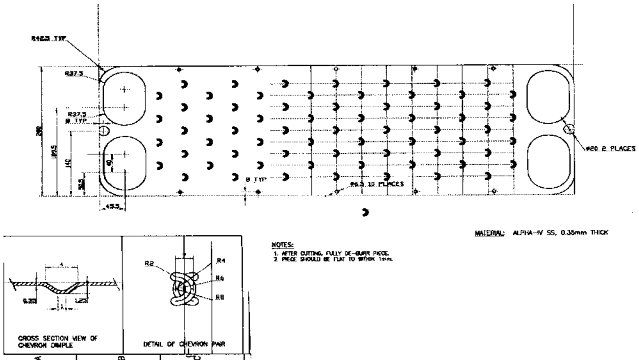


Figure 7 20 kW Natural gas dimpled plate air heat exchanger thin plate

In Gas class Thermodynamic properties of gases are calculated by using perfect gas equations and partial continuous specific heat equations.

$$Cp_i(T) = A_i + B_i*10^{-3}*T + C_i*10^{5}/T^{2} + D_i*10^{-6}*T^{2}$$
$$T_{Hi} < T <= T_{Li} \qquad (1)$$

A_i, B_i, C_i, D_i, are equation coefficients for the temperature range T_{Li} and THi. Enthalpy, entropy and Gibbs free energy are determined by using standard thermodynamic equations from the given specific heat equation. For example enthalpy can be calculated from partial continuous Cp equations as:

$$h(T) = (\sum_{i=1}^{N-1} \int_{TLi}^{THi} Cpi(T).dT) + \int_{TLi}^{T} Cpi(T)dT \quad (2)$$

Data of viscosity and thermal conductivity are calculated from polynomial equations.

$$k(T) = \sum_{i=0}^{N} ka_i \cdot T^i \qquad (3)$$

$$\mu(T) = \sum_{i=0}^{N} ma_i \cdot T^i \qquad (4)$$

Prantl number is also calculated in this class from these properties

$$Pr(T) = Cp(T).\ \mu(T)/k(T) \qquad (5)$$

This class is also know atomic composition and properties of the gas through the subclass Atom.

Gmix : Thermo physical properties of ideal gas mixtures(Enthalpy is the function of temperature, entropy function of temperature and pressure) including viscosity, Prandtl number and Thermal conductivity is calculated in this class. The mixture properties are basically calculated by using linear volumetric mixing rules, except in viscosity and thermal conductivity, Wilke (1950)[1] equations are used.

$$\mu_{mix} = \sum_{i=1}^{n} \left((x_i\mu_i) / \sum_{j=1}^{n} (x_j\phi_{ij}) \right) \qquad (6)$$

$$\phi_{ij}=(1+(\mu_i/\mu_j)^{1/2}(M_j/M_i)^{1/4}))^2/(8+8M_i/M_j)^{1/2}) \qquad (6\ a)$$

In this formula, M_i is the molecular weight; x_i is the mole fraction.

Pipe : pipe and tube flow including various geometries, self flow condition determination, such as friction factor, mode of the flow Reynolds number, convective heat transfer coefficient inside of the pipe is calculated by using this class. The pipe class uses the gas mixture properties through the subclass Gmix. The friction factor is calculated by using critical Reynolds Number concept.

$$Re = \rho(T,P)\ U_m\ D_H / \mu\ (T,P) \qquad (7)$$

Critical Reynolds number is assumed to be equal to 2300. The pipe class assumed Laminar flow below this value. For laminar Flow

$$f = C/Re(T,P) \qquad (8)$$

Where C is a shape dependent factor. For example for the circular pipe is equal to 64. In the heat exchanger modelling rectangular channels are used. In this kind of geometry, it is a changing variable of channel width and height. For the flow above the model assumes critical turbulent flow and friction coefficient is calculated by using turbulent model. In this model friction factor is determined by solving Colebrook's equation

$$g(T,P) = 1/\sqrt{f} + 2.0$$

$$\log_{10}(((\varepsilon/D_H)/3.7+2.51/(Re(T,P)\sqrt{f}\ )) = 0 \qquad (9)$$

In this equation ε is the surface roughness, D_H is the hydraulic diameter. This is a non-linear equation and it should be solved to obtain a value for friction factor. Newton-Raphson method is used to solve this equation. This method solve iteratively by using equation 10.

$$f_i(T,P) = f_{i-1}(T,P) - g(T,P) / (dg(T,P)/df(T,P)) \qquad (10)$$

In order to determine the initial conditions equation 11 is used.

$$f(T,P)=1.325/(\log_e((\varepsilon/D_H)/3.7+5.74/Re(T,P)^{**}0.9))^{**}2 \qquad (11)$$

Pressure drop of the pipe can also be calculated from

$$dP= f(T,P)/D_H * dX * U(T,P)* U(T,P) / 2 \qquad (12)$$

In this equation dP indicates the pressure drop, D_H is hydraulic diameter, U(T,P) is the velocity and dX is the length of the pipe.

Internal heat transfer coefficient, like friction is the function of critical Reynolds number. For laminar flow, it changes only as a function of the channel (pipe) geometry; geometrical factor is calculated through polynomial curve fittings. For Turbulent flow Gnielenski equation is used

$$Nu=f/8*(Re-1000)*Pr/(1+12.7*(f/8)^{0.5}*Pr^{2/3}-1)) \qquad (13)$$

For turbulent flow different cross sections are represented by using hydraulic diameter concept.

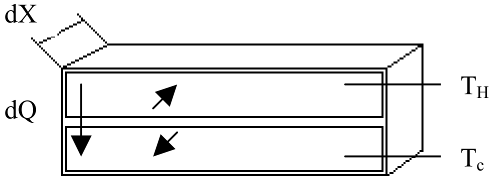


Figure 8 rectangular heat exchanger, Plate_HE, model physical layout

Plate_HE: this class simulates rectangular channel, flat plate heat exchanger.Plate heat exchanger is made of rectangular channels. Simulation model is capable of calculating both parallel and counter flow of the gas mixtures.

Basic channel thermodynamic and flow properties are calculated in sub class pipe. Calculations are done in finite difference basis. Total length of the heat exchanger is divided to n small pieces. For each small section all properties can be assumed to be constant. For this section heat transfer from hot gas mixtures to the cold gas mixture can be written as:

$$dQ=Q_{hot\text{-}in} - Q_{hot\text{-}out} = Q_{cold\text{-}out} - Q_{cold\text{-}in} = Q_{heat\ transfer} \quad (14)$$

$$dQ=U^{*}dA^{*}(T_{hot\ gas} - T_{cold\ gas}) \quad (14a)$$

$$dQ= m_{hot\ gas\ mixture}{}^{*}(h_{hot\ gas\ -in} - h_{hot\ gas\ -\ out}) \quad (14b)$$

$$dQ= m_{cold\ gas\ mixture}{}^{*}(h_{hot\ gas\ -in} - h_{hot\ gas\ -\ out}) \quad (14c)$$

Where U is the overall heat transfer coefficient, dA is the heat transfer area, h is the enthalpy of the gas. When the set of equation 14 is solved. Enthalpy of the next step is calculated and from the enthalpy temperature of the next step is determined.

This process is continued to determine the temperature profile for the whole heat exchanger. For these calculations initial values of the heat exchanger temperatures are required. In some heat exchangers known temperatures for hot and cold gases could be in opposite side of the heat exchanger. In this case for unknown value, some input values are assumed at x=0 and temperatures at x=L is calculated. By using bisection equation solving method between inlet (x=0) and outlet (x=L) values and actual value at the exit, actual inlet conditions are calculated. . In case of two side of heat exchanger temperature is given, bisection non-linear equation solution method is used to calculate mass flow rate ratio of this fluid. By using the results of the simulations actual heat exchangers are designed. In figure 6 an actual plate designs of the 1.5 KW fuel site counter flow heat exchangers is shown.

Dimpled_plate_HE: rectangular channel dimpled plate heat exchanger. Dimple plate heat exchangers are similar to the plate heat exchangers, but due to the dimples in the flow patterns, flow is more complicated. In this model each dimple location and the dimple radius is defined, and flow conditions around these restrictions are calculated. A dimpled Heat exchanger plate is shown in Figure 7. It should be also noteted that heat transfer equations given for the flat case is not valid here. A more complicated model is used.

A steady state performance of an air heat exchanger is shown in figure 9. The temperature profile obtained from the actual heat exchanger designed from these simulation models were close to the simulation model.

TimeD_HE: After the actual design criterias are determined, more complicated (time dependent) method of calculations is also used to check stability of the heat exchangers. After the initial design, we have an accurate figure for total heat exchanger mass. When the heat exchanger control valve is opened or close by the system requirements automatically, time response of the heat exchanger can be calculated and required time controls and thermal stability of the system can be checked.

ENHANCING HEAT TRANSFER OPERATIONS BY ACTIVE CONTROLS

All the heat exchanger temperature profiles are actively controlled by PLC programs. PLC Programs are connected to a real time control software language called CİTECT. By using this software all the heat exchangers and system parameters can be controlled or changed according to needs arise. All this functions can be controlled also from distance.

OTHER ENERGY ENHANCING DEVICES

Adiabatic and internal (isothermal) reformers are used to change fuel. A nickel base low temperature carbon-water shift reaction catalyst is used to convert fuel adiabaticaly.

Fuel conversion occurs according to

Reaction catalyst force reaction to equilibrium condition, which can be calculated numerical by minimizing Gibbs free energy equation.

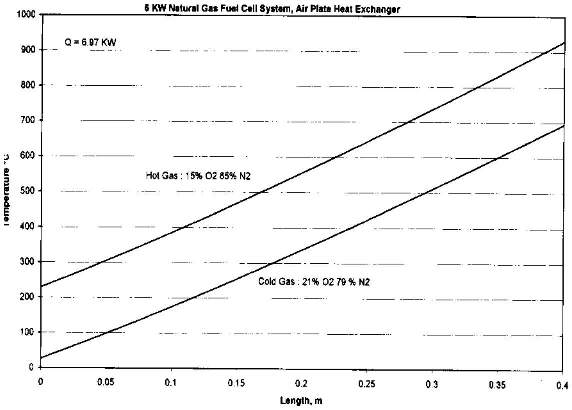


Figure 9 5 KW Natural gas air heat exchanger performance

$C_nH_m + n\ H_2O = n\ CO + (n + m/2)\ H_2$

First stage reforming occurs at 500°C inlet and approximately 300°C exit conditions. Reaction should occur ideally at constant temperature (isothermally), but difficulty of creating a heat exchanger with the load of catalyst forced us to work in adiabatic conditions.

A Catalytic reactor is used to combust any uncombusted fuel and utilise the energy created to evaporate steam needed in adiabatic reformer. For low fuel flow rates catalytic reactors are ideal devices to burn the gases. But when too much gases passes through the fuel cell system unburned, it creates problem. Catalytic converter temperature should be limited to 800°C to avoid metal core destructions. Air to fuel ratios should not also fell self-explosion ranges. A careful analysis and models of these devices are carried out. It is shown that, they cannot be made 100% safe, but quite a high safety factor can be achieved.

A water evaporator is used to raise steam required by the system. As a simple first system, a tube and shell type evaporator is used. In this evaporator, water flowed inside of the tubes, while hot combustion gases aware flowing from outside. Difficulty of this system was the possibility of the fouling. To ensure not to plug the tubes, water is purified in the 1.5 KW experimental set-up. In the next stage, to be able to work only with treated water a two stage boiler and super heater is designed.

Heat recovery heat exchangers are used to recover energy left in the exhaust gas stream. A simple shell and tube heat exchanger is used for this stage. Performance of this heat exchanger was satisfactory.

FUTURE DEVELOPMENTS

One of the considerations for the gas-gas heat recovery systems could be new controlled porous metal structure. This natural internal fin structures could allow high heat transfer coefficient with lower costs at very high temperature heat transfer applications. An isothermal reformer should be developed. Any idea of compact heat exchanger with loading a reloading of catalyst capabilities is welcomed. New enhanced evaporator designs should be applied to water evaporator. Fuel cell itself required some further developments to achieve better heat transfer between internal reforming and heat generation regions.

CONCLUSIONS

Solid oxide fuel cells can be future energy conversion devices. They have very high efficiencies compare to classical energy conversion technologies. They are also more environmentally friendly due to negligible nitrous oxide and sulphur oxide compounds. Because of the high efficiencies, their total CO2 emission to the atmosphere will be less. With a huge start up market available for the technology, more work on fuel cell energy recovery systems will be pay off easily.

NOMENCLATURE

A_i, B_i, C_i, D_i : coefficients of C_{Pi}
C_{Pi}: specific heat between temperatures T_{Li}, T_{Hi}
dA : the heat transfer area of the small heat exchanger section
dg(T,P)/df(T,P) : derivative of Colebrook's equation
dX : the length of small heat exchanger section
f: friction factor
g(T,P) Colebrook's equation
h: enthalpy
k: thermal conductivity
ka_i : coefficients of thermal conductivity equation
ma_i: coefficients of viscosity equation
m = mass flow rate of the gas mixtures flowing in the heat exchangers
μ : viscosity
Nu(T,P) : Nusselts number
Pr(T) : Prantl number
Re(T,P) Reynolds number
T_{Li}, T_{Hi} : temperature range for C_{pi} equation
T: temperature
x_i: molar ratio of the ith gas
U : overall heat transfer coefficient

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1. Wilke C. R. (1950) J. Chem. Phys., vol. 18, pp. 518-519
2. Galielinski, V., Int Chem Eng., 16, 359, 1976