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Separation and recovery of carbon dioxide by a membrane flash process utilizing waste thermal energy

Kazuhiro Okabe*, Satoshi Kodama, Hiroshi Mano, Yuichi Fujioka

Research Institute of Innovative Technology for the Earth (RITE)

Abstract

The membrane flash process utilizing waste thermal energy was developed to realize an energy-saving technology and to substitute it for a conventional regenerator. The operating conditions of a membrane flash at high temperature were studied. The DEA concentration and the flashing pressure had optimum values to improve the performance and reduce the energy consumption for CO₂ recovery. The petroleum refinery process and iron manufacturing process were proposed for candidate processes that actually had waste energy sources. Energy consumption and costs for CO₂ recovery in the membrane flash and chemical absorption were estimated by custom-made program and discussed under the same conditions. The membrane flash was suitable for the CO₂ emission sources that had high CO₂ concentration independently of the plant scale. The chemical absorption was suitable for large-scale sources, even if the CO₂ concentration was low.

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1. Introduction

The developments of renewable energies and energy-saving technologies are advanced as countermeasures against global warming, however it is difficult to convert from present energy sources to these in a short period. Therefore, focus has been placed on CCS (carbon capture and storage) technology, and pilot plant tests are carried out in several places. Not only developing CCS technology, but also reducing its cost is necessary for applying CCS to practical use as one of the measures for preventing global warming. The principal cost of CCS consists of carbon dioxide (CO₂) capture, transport and injection, and there is a demand to decrease the cost of capture because it occupies a large portion of the total cost of the CCS process.

The Research Institute of Innovative Technology for the Earth (RITE) has been developing a novel process called a membrane flash process. This process was proposed by Teramoto et al. [1,2,3]. We have been studying the modification and improvement of this process to substitute it for a conventional regenerator. The following results have been obtained through our research up until now [4,5]. Aluminum oxide was the most suitable membrane

* Corresponding author. Tel.: +81-774-75-2305; fax: +81-774-75-2318.
E-mail address: okabe@rite.or.jp.

material for this process. The electric energy for CO₂ recovery was lower than the thermal energy of the chemical absorption process. Flashing at elevated temperature significantly reduced the electric energy and required much less membrane area, so that this process has potentiality to realize low cost technology for CO₂ capture when waste thermal energy can be utilized to elevate the flashing temperature.

In the present study, the operating conditions of absorbent concentration and flashing pressure were studied using aluminum oxide for a membrane material, and diethanolamine (DEA) for an absorbent to improve the performance of the membrane flash process. The petroleum refinery process (PSA off gas) and iron manufacture (blast furnace gas) were proposed for candidate processes which actually had waste energy sources. The experimental data were applied to these processes, and energy consumptions and costs for CO₂ recovery by the membrane flash and chemical absorption were estimated and discussed under the same conditions.

2. Methodology

2.1. Experimental

The experimental conditions are shown in Table 1. Aluminum oxide tubes (Al₂O₃; NGK Insulators, Ltd.) were used as the membranes, and aqueous diethanolamine (DEA) solutions were examined as the CO₂ absorbent solutions. Carbon dioxide and nitrogen (N₂) mixed gas with saturated water vapor was used as a simulated flue gas. The performances were measured varying flashing pressure and concentration of DEA.

Table 1 Experimental conditions

Membrane	Material : Aluminum oxide Tube diameter : inside 7.0 mm, outside 10 mm Pore size : 14 μm Membrane area : 13 cm ²
Absorbent solution	Aqueous diethanolamine solution [HN(CH ₂ CH ₂ OH) ₂] Concentration : 2, 3, 4, 5 mol/l
Simulated flue gas	CO ₂ : 15 % N ₂ : balance (with saturated water vapor at 40 °C)
Temperature	Absorption : 40 °C Flashing : 70 °C
Pressure	Absorption : 115 – 120 kPa Flashing : 30 to 46 kPa (including water vapor pressure at 70 °C)

The schematic diagram of the experimental setup is shown in Figure 1. The simulated flue gas was synthesized by mixing each gas, whose flow rate was controlled by a mass flow controller. The simulated flue gas was supplied to an absorber at a pressure slightly higher than the atmospheric pressure. The absorbent solution was also supplied to the absorber by a liquid circulation pump and it became rich solution. The rich solution was heated at 70 °C before the module and fed to the inner side of the aluminum oxide tube in the module by another circulation pump. The outer side of the tube was evacuated at the low pressure P_F . P_F included the CO₂ partial pressure P_{CO_2} and water vapor pressure P_W . P_F was controlled at about 30 to 46 kPa and P_W was assumed to be the saturated water vapor pressure P_W^* at the operating temperature. Most of the rich solution permeated and flashed through the membranes, and then the rich solution released CO₂ to become a lean solution. A small amount of rich solution flowed through the inside of the tube and overflowed at the top of the module, then it returned to a liquid reservoir. The lean solution and released gas returned to the reservoir in which they were cooled at 40 °C and the solution was recycled to the feed side. The released gas was passed through a condenser and it was discharged from a vacuum pump. Its flow rate was measured by a digital soap-film flow meter and the gas composition was determined by a gas chromatograph (Varian, CP-4900) with two kinds of columns, which were a Porapak Q for CO₂ and N₂ analysis, and a molecular sieve 5A for N₂ and O₂ analysis to compensate for air leakage. The performances were calculated

from these data. The electric energies of major equipments were calculated by the similar method described in the previous report [5].

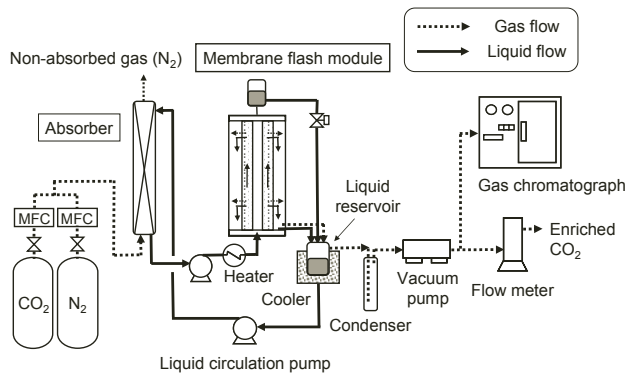


Figure 1 Schematic diagram of experimental setup

2.2. Energy and cost estimation

We investigated several industrial processes such as in the petrochemical industry, iron manufacturing industry, cement industry, paper industry, etc. focusing on whether they were CO₂ emission sources and also whether they had available waste heat sources for elevating flashing temperature. As a result, it was found that petroleum refining and the iron manufacturing were possible processes for CO₂ recovery by the membrane flash process. A product such as light oil through the desulphurization process still has residual heat of about 120 °C even after the heat recovery process. In iron manufacturing, the blast furnace gas is one of the CO₂ sources, and the sensible heat of blast furnace slag is thought to be a possible waste heat source.

A flowchart of the membrane flash process utilizing a waste heat source is shown in Figure 2. The absorber is the same system as that of the chemical absorption process. The rich solution passes through a pre-heat-exchanger to recover thermal energy from the lean solution. After that, it is heated by the waste heat source to the appointed temperature and then fed to the module. The lean solution that passes through the pre-heat-exchanger is cooled by cold water, and returns to the absorber.

The exhaust gas from PSA equipment for hydrogen recovery in a petroleum refining process and the blast furnace gas in iron manufacturing were selected for the objects of process estimation. The flue gas from a coal-fired power plant was also added to the estimation for the reference. The properties of those gases are shown in Table 2.

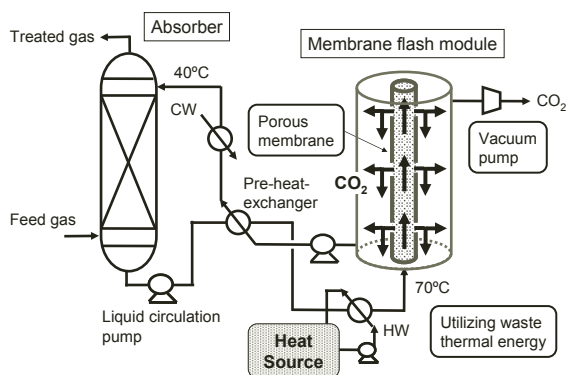


Figure 2 Flowchart for utilization of waste thermal energy

Table 2 Property of emission gas

CO ₂ emission source	PSA off gas (Petroleum refinery)	Blast furnace gas (Iron manufacture)	Combustion gas (Coal fired power plant)
Total gas emission [Nm ³ h ⁻¹]	5,000	800,000	1,700,000
CO ₂ concentration [%]	44	22	15
Pressure [kPaA]	Atmosphere	107	Atmosphere
Gas temperature [°C]	30	35	50

Table 3 Calculation conditions

	Membrane flash	Chemical absorption
Absorbent solution	Aqueous diethanolamine solution [HN(CH ₂ CH ₂ OH) ₂] Concentration : 2, 3, 4, 5 mol/l	Aqueous monoethanolamine solution [H ₂ NCH ₂ CH ₂ OH] Concentration : 5 mol/l
Absorption Temperature	40 °C	40 °C
Pressure	120 kPaA	243 kPaA
Stripper Temperature	70 °C	about 107 °C
(Flash) Pressure	34 kPaA (Experimental data)	about 121 kPaA (Calculated through mass balance and heat balance)
Recovery ratio	80 %	90 %
Temperature of waste energy source	120 °C	-

Energy and cost for CO₂ recovery were estimated by a custom-made program for a membrane flash process. In this program, the release rate coefficient, which was defined by the following equation (1), was taken in the process simulation to represent the performance of a membrane flash process, because it was not established to express this phenomenon as a physicochemical model.

$$k = V_{CO_2} Q_{CO_2}^{-1} \Delta\alpha^{-1} \quad (1)$$

Here, k is the release rate coefficient, V_{CO_2} is the amount of released CO₂ [mol (m² h)⁻¹], Q_{CO_2} is the amount of CO₂ which is included in the liquid that permeates through the membrane during releasing V_{CO_2} [mol (m² h)⁻¹], α is the CO₂ loading [mol of CO₂/mol of amine], and $\Delta\alpha$ is the difference between loading of a rich solution and assumed loading of the solution equilibrated with CO₂ partial pressure in the membrane module. The release rate coefficient k was calculated by experimental data.

Similar estimations for chemical absorption using monoethanolamine (MEA) were performed under the same assumptions. The calculation conditions are listed in Table 3. Other parameters such as temperature, pressure, flow rate, etc. were provided by experimental data.

3. Results and discussion

3.1. Performance of the membrane flash method

It was reported that the overall mass transfer coefficient was proportional to the liquid flow rate, and the module performance was represented by the proportional constant, which is the amount of released CO₂ per unit liquid flow rate [5]. The flashing performances K_F , which were measured by varying the flashing pressure P_F and concentration of DEA C_{DEA} , are shown in Figure 3. K_F is represented by the ratio of released CO₂ U_{CO_2} [m³ (m² h)⁻¹] to liquid flow

rate U_L [$\text{m}^3 (\text{m}^2 \text{h}^{-1})$]. K_F was increased with increasing C_{DEA} up to 4.0 mol/l, then it decreased at 5.0 mol/l. At the high pressure P_F , K_F decreased and the extent of decrease was large in the high C_{DEA} solution. It is supposed that the driving force of CO_2 release decreased in the high C_{DEA} solution because the equilibrium absorption of CO_2 was lower in the high C_{DEA} solution so that the loading of rich solution was lower, then the loading difference $\Delta\alpha$ became low. K_F also decreased even at the low pressure P_F in 4.0 and 5.0 mol/l solutions. The experimental results indicated that the absorbent solution flowed proportional to P_F , however U_{CO_2} did not increase proportional to P_F at the low P_F . It was assumed that P_{CO_2} did not reach the fixed pressure in the experiments at the low P_F .

The electric energies E_e of major equipment, which were described for recovering 1 kg CO_2 , are shown in Figure 4 for each C_{DEA} vs. flashing pressure P_F . Those energies were calculated from the data of Figure 3 on the basis of overall material balance and overall heat balance. E_e was well correspondent to the performance K_F , and E_e was the lowest when C_{DEA} was 4.0 mol/l and P_F was 34 kPa, which was the pressure resulting from adding about 5 kPa to the P_W^* , in the present study. The performance of the membrane flash K_F was improved about two times, and the electric energy E_e was reduced to about 60% compared with a conventional DEA solution of 2.0 mol/l.

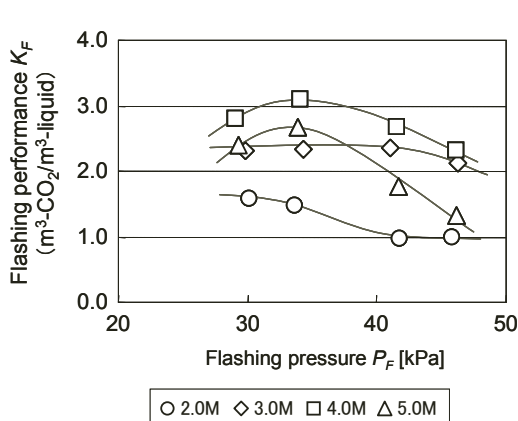


Figure 3 Flashing performance K_F vs. P_F and C_{DEA}

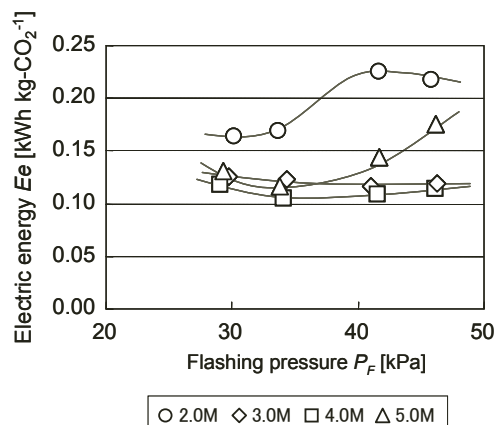


Figure 4 Electric energy of major equipments E_e vs. P_F and C_{DEA}

3.2. Application of a membrane flash and chemical absorption for petroleum refining

The application of a membrane flash process and a chemical absorption process for CO_2 separation from the exhaust gas of PSA equipment in a petroleum refining process was studied. The process calculations were carried out by a custom-made program on the basis of experimental data. Energy items are shown in Figure 5. Electric energy for the membrane flash is shown on the left, and thermal energy for chemical absorption is shown on the right. They can be converted to each other on the assumption that the efficiency of electric power generation is 40%. The DEA solutions of 2.0 to 5.0 mol/l are tested in this process. The total energies of chemical absorption by monoethanolamine (MEA) solution and KS-1 solution [6] are also shown in Figure 5. The total energy of the membrane flash decreased with increasing C_{DEA} . The energy consumption of a vacuum compressor was relatively large in all C_{DEA} solutions. The thermal energy of chemical absorption by MEA solution was calculated at 3.6 to 4.3 GJ ton-CO_2^{-1} described later in Figure 9. These results almost agree with the literature data, which were calculated by ASPEN Plus at 4.1 to 4.3 GJ ton-CO_2^{-1} [7] and at 4.0 to 4.9 GJ ton-CO_2^{-1} [8], so the custom-made program seems to work appropriately for process calculation. The electric energies of the membrane flash except waste heat energy were lower than the thermal energies of chemical absorption by both MEA and KS-1 solutions.

The waste heat energies at each C_{DEA} calculated by the custom-made program are shown in Figure 6. The electric energies converted to the unit of GJ ton-CO_2^{-1} were also described in Figure 6. The waste heat energy was considerably larger than the electric energy of the membrane flash, and it was a little larger than the thermal energy of chemical absorption. However the waste energy cost for the membrane flash of the total CO_2 recovery cost does

not need to be taken into account, because the waste energy is the heat left behind after the available thermal energy has already been recovered, or its temperature is too low from the first to utilize it for other purposes.

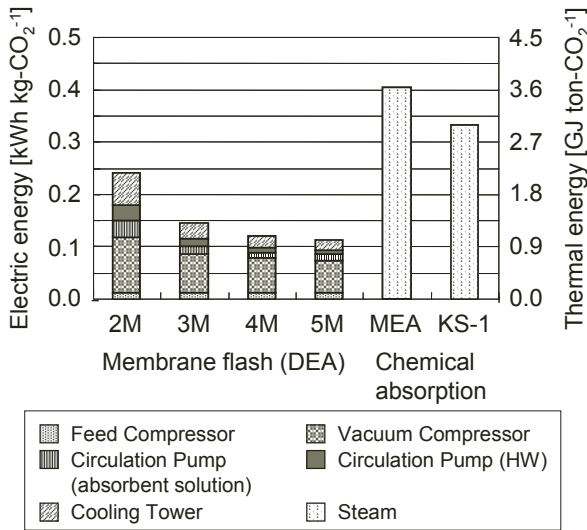


Figure 5 Energy items for major equipments

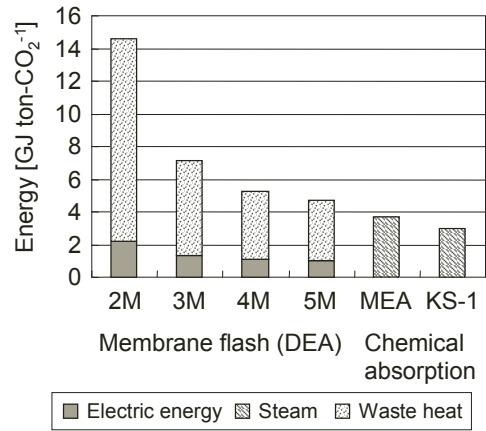


Figure 6 Heat energy for membrane flash and chemical absorption

3.3. Application of a membrane flash for iron manufacturing and an electric power plant

The application of a membrane flash process for CO₂ separation from a blast furnace gas and a flue gas was studied. The process calculations were carried out by a custom-made program. The electric energies vs. C_{DEA} are shown in Figure 7, and the costs for CO₂ recovery are shown in Figure 8. The electric energies increased rapidly at the low C_{DEA} in all cases. The costs had similar dependence on C_{DEA} as the energies. The cost in the flue gas case is higher than in the other two cases, so the cost was strongly dependent on the CO₂ concentration in the feed gas.

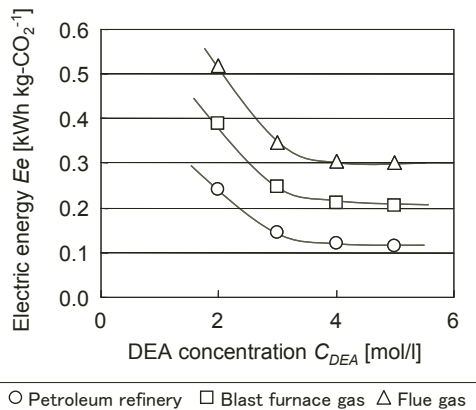


Figure 7 Electric energy of membrane flash in industrial process

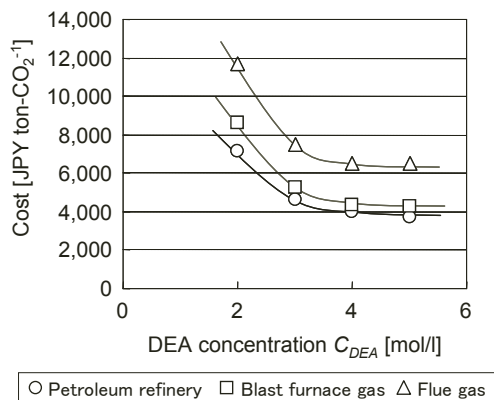


Figure 8 Cost of membrane flash in industrial process

3.4. Comparison of energy and cost in a membrane flash and chemical absorption

The dependence of energy on CO₂ concentration of feed gases for the membrane flash ($C_{DEA}=5$ mol/l) and chemical absorption were shown in Figure 9. Electric energy for the membrane flash is shown on the left, and thermal energy for chemical absorption is shown on the right. Each CO₂ concentration is corresponding to each CO₂ emission source listed in Table 2. The energy for chemical absorption using KS-1 solution at the CO₂ concentration of 15% was also described in Figure 9. The electric energies of the membrane flash are considerably smaller than that of chemical absorption using MEA solution. The dependence of energy on CO₂ concentration was larger in the membrane flash than in chemical absorption. The energies of the membrane flash and chemical absorption using KS-1 solution were almost the same at the CO₂ concentration of 15%. As a result of these calculations, it was found that the application for the CO₂ emission source with high CO₂ concentration gas can realize the low energy capture in both a membrane flash and chemical absorption.

The dependence of cost on CO₂ concentration of feed gases for the membrane flash and chemical absorption were shown in Figure 10. The cost of the membrane flash is lower at high CO₂ concentration, and increased sharply at low CO₂ concentration even though the plant scale was larger. The scale merit of the plant did not appear in the cost of the membrane flash, considering the amount of emission gas in each process. On the other hand, the cost of chemical absorption had a minimum value. The high cost at high CO₂ concentration is thought to be caused by the small scale of the petroleum refinery. The cost at low CO₂ concentration increased though the plant scale is large. It results from the low CO₂ concentration. As a result of cost estimation, the low cost capture is realized in a membrane flash when it is applied for the CO₂ emission source with high CO₂ concentration gas independently of the plant scale. In chemical absorption, the low cost capture is realized when it is applied for the large-scale emission source, with still more advantage in the high CO₂ concentration gas.

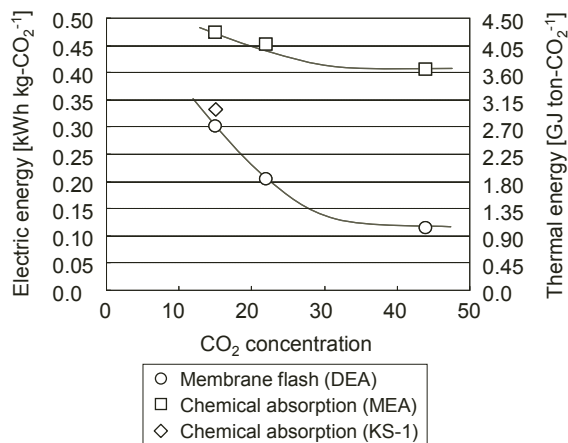


Figure 9 Electric energy of membrane flash and chemical absorption

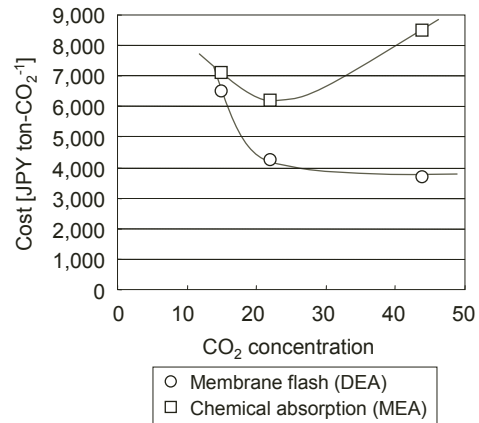


Figure 10 Cost of membrane flash and Chemical absorption

4. Conclusion

The operating conditions were studied to improve the performance of the membrane flash process. Energy consumptions and costs for CO₂ recovery by the membrane flash and chemical absorption were estimated in petroleum refining, iron manufacturing and a coal fired power plant. As a result, the following conclusions were obtained.

1. The 4.0 mol/l solution was the optimum concentration in C_{DEA} and 34 kPa was the optimum pressure in P_F . The performance was improved about two times and the energy consumption was reduced to about 60% under that conditions.
2. In both the membrane flash and chemical absorption, the low energy capture is realized when it is applied for the CO₂ emission source with high CO₂ concentration gas.

3. The membrane flash can economically capture CO₂ at the emission source with high CO₂ concentration gas independently of the plant scale.

4. Chemical absorption can economically capture CO₂ at the large-scale emission source, still more advantage in the high CO₂ concentration gas.

Acknowledgements

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Nomenclature

P_F	Flashing pressure [kPa]
P_{CO_2}	CO ₂ partial pressure [kPa]
P_W	Water vapor pressure [kPa]
P_W^*	Saturated water vapor pressure [kPa]
k	Release rate coefficient
V_{CO_2}	Amount of released CO ₂ [mol (m ² h) ⁻¹]
Q_{CO_2}	Amount of CO ₂ in the liquid [mol (m ² h) ⁻¹]
α	CO ₂ loading [mol of CO ₂ / mol of amine]
$\Delta\alpha$	Loading difference between a rich solution and the equilibrated solution with CO ₂ partial pressure in the membrane module.
C_{DEA}	Concentration of DEA
U_{CO_2}	Amount of released CO ₂ [m ³ (m ² h) ⁻¹]
U_L	Liquid flow rate [m ³ (m ² h) ⁻¹]
E_e	Electric energy of major equipments

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