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THEMATIC SECTION: LOW EMISSION STEELMAKING

Sustainable Aspects of Ultimate Reduction of CO_2 in the Steelmaking Process (COURSE50 Project), Part 2: CO_2 Capture

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Abstract COURSE50 (ultimate reduction of CO_2 in the steelmaking process through innovative technology for Cool Earth 50) aims to capture, separate, and recover CO_2 from blast furnace gas. From a practical realization viewpoint, three points are important. The first is energy consumption to regenerate the absorbent, second is the energy cost of the heat for regeneration, and third is the facility cost. The advantage afforded by the COURSE50 approach in relation to the CO_2 capture process is the utilization of unused waste heat from the steel mills. Energy consumption to regenerate the absorbent is determined mainly by three factors: the regeneration reaction determined primarily by the structure of the chemical absorbent, the energy required to heat that volume of absorption liquid, which is affected by the absorption rate of the agent, and the heat loss from the processes. The most influential factor is the energy required for the regeneration reaction. We discovered high-performance absorbents with the advantages of high absorption rates, high cyclic capacities, and low heats of reaction, and we then compared these with monoethanolamine (MEA) and N-methyldiethanolamine (MDEA). The newly discovered absorbents performed well in terms of absorption rates and cyclic capacities. Among these absorbents, some showed lower heats of reaction than MDEA. These results provide a basic guideline for the discovery of potential amine-based absorbents that may lead to the development of new absorbent systems for CO_2 capture.

Keywords CO_2 emissions mitigation · Steelworks · Separation and recovery of CO_2 from blast furnace gas · Unused exhaust heat in steelworks

Preface

Overview

We have executed technology development through an innovative R&D program, the COURSE50 project [1, 2]. This project, which commenced in fiscal 2008, aims to mitigate CO_2 emissions from integrated steel plants. Figure 1 presents an outline of the COURSE50 project and the two major areas of research.

One area is the development of technology to reduce CO_2 emissions from blast furnaces, involving (1) reaction control technology to reduce iron ore by using hydrogen, (2) reforming technology for coke oven gas (COG) that increases the amount of hydrogen produce, and (3) technology to manufacture high-strength and high-reactivity coke for hydrogen-reduction blast furnaces.

The other area is the development of technology to capture CO_2 from blast furnace gas (BFG) through chemical absorption and physical adsorption methods using unused waste heat in the steelworks. The final objective is

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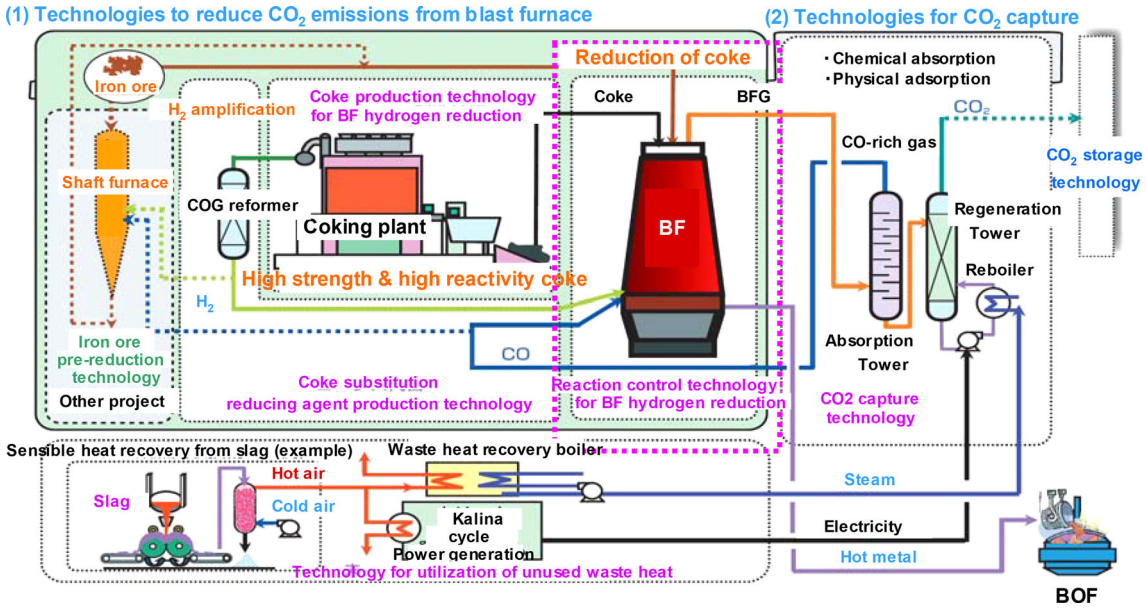

Fig. 1 Outline of COURSE50 [3]

to reduce CO_2 emissions from the steelworks by approximately 30 %. The development of the fundamental technologies in Step 1 (2008–2012) was completed as per the project schedule, and now, the development of integrated technologies based on the results of the fundamental technologies is being promoted in Step 2 (2013–2017).

The typical process flow for chemical absorption is shown in Figs. 2 and 3. (1) First, the absorbent comes into contact with the feed gas in the absorber counter-currently and selectively absorbs CO_2, and (2) then, the CO_2-rich absorbent is sent to the stripper where the CO_2 is released by heating at about 120 °C. (3) Finally, the regenerated absorbent is cooled and sent back to the absorber to repeat the cycle.

CO_2 recovery systems mainly utilize either the chemical absorption method or physical adsorption method (for example, PSA and VPSA). Unused waste heat from the

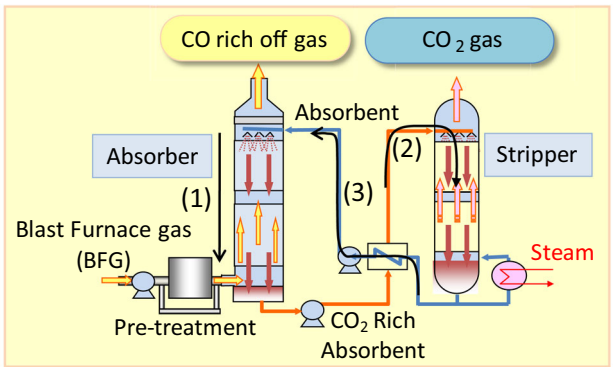

Fig. 2 Chemical absorption process [3]

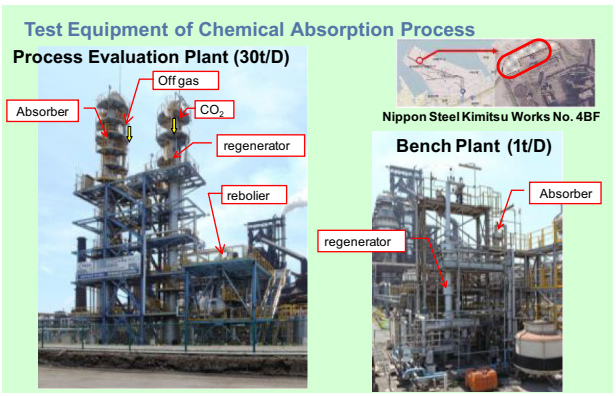

Fig. 3 Chemical absorption process

steelworks can be converted into steam and used to regenerate the chemical absorbent or to generate the power needed for physical adsorption. Power generation efficiency is a function of the temperature of the heat source, as shown in Fig. 4. Therefore, the heat source temperature and the quantitative level of unused waste heat determine the optimum configuration.

Approach to Optimize CO_2 Mitigation of Chemical Absorption

In order to estimate the total cost of chemical absorption, an estimate was made as presented in Figs. 5, 6, and 7. The energy of the chemical reaction was determined through laboratory experiments, and the sensible heat and heat loss from the process were derived from the results of the pilot

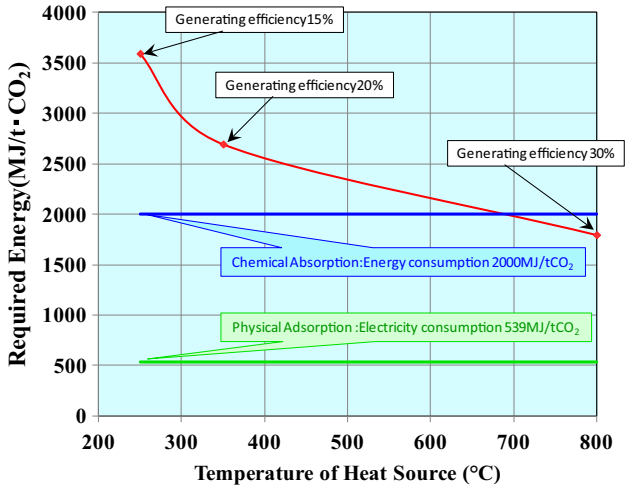

Fig. 4 Influence of Heat Source Temperature on the Required Energy [3]

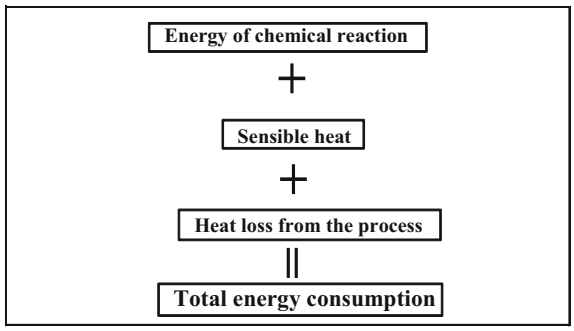

Fig. 5 Estimation of total chemical absorption cost (1)

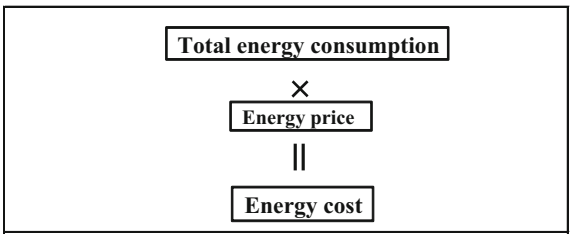

Fig. 6 Estimation of total chemical absorption cost (2)

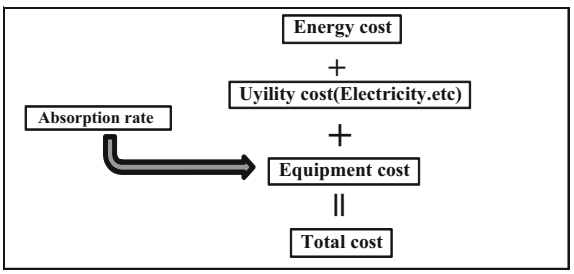

Fig. 7 Estimation of total chemical absorption cost (3)

plant (30 t/d) operation, as tabulated in Table 1. The energy price was determined by summing the fixed and variable costs required for the utilization of unused exhaust heat. The utility cost was based on the cost to operate the pilot plant (30 t/d).

The equipment cost of the absorption tower was determined by the absorption rate of each chemical absorbent. Using the absorption rate data, the facility costs were estimated as follows:

(1) The residence time of the absorption liquid was determined using the gas flow rate and other properties of the gas and absorbent.
(2) The gas flow rate was determined by the facility capacity and tower diameter.
(3) The tower height was determined by the absorption rate of each absorption liquid, and the tower diameter was determined by the required tower productivity.

The equipment cost of the regeneration tower was determined in proportion to the total energy consumption of the regeneration tower. The other equipment costs were estimated proportionally to the cost of both towers.

Table 1 and Fig. 8 show examples of absorbent properties, and Table 2 shows the prerequisites for the estimate.

Technology to Capture CO_2 from Blast Furnace gas

Chemical Reaction Heat

Commercially available amine absorbents have been broadly investigated by a number of researchers [4–11]. A new class of amines referred to as sterically hindered amines, such as 2-amino-2-methyl-1-propanol (AMP) and 2-Piperidineethanol (2-PPE), have been proposed as commercially attractive new solvents for treating acid gas and to replace existing commercial amines such as monoethanolamine (MEA), diethanolamine (DEA), 2-(ethylamino)ethanol, (EAE), and N-methyldiethanolamine (MDEA) [6, 12]. Seven hindered amine absorbents with a particular modification to their chemical structures were synthesized and investigated. In addition, eleven commercially available amine absorbents were investigated.

Various amine absorbents [13, 14] were evaluated for their CO_2 loading capacity, heats of reaction and absorption rates in comparison to MEA, DEA, and MDEA, and a structure–performance relationship was found to exist. The relationship between heat of reaction and CO_2 absorption rate, as determined experimentally, for a primary MEA, secondary amine DEA, and tertiary amine MDEA are shown in Fig. 9.

Table 1 Estimate for chemical absorption process

Absorbent A (example)		
Absorption amount	g-CO_2/L-soln.	146.3
Cyclic cap. ratio (cycle capacity/absorption amount)		0.8
Specific liquid circulation rate	L/kgCO_2	8.54
Required heating temperature	K	8
Heat capacity	Joule/(gK)	3.8
Required energy consumption for heating	GJ/tCO_2	0.26
Required energy consumption for chemical reaction	GJ/tCO_2	1.50
Latent heat of exhaust gas	GJ/tCO_2	0.21
Total required energy	GJ/tCO_2	1.97

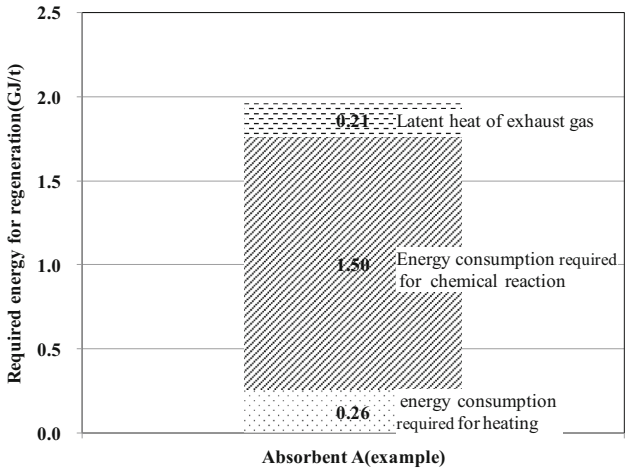

Fig. 8 Schematic image of energy required for regeneration

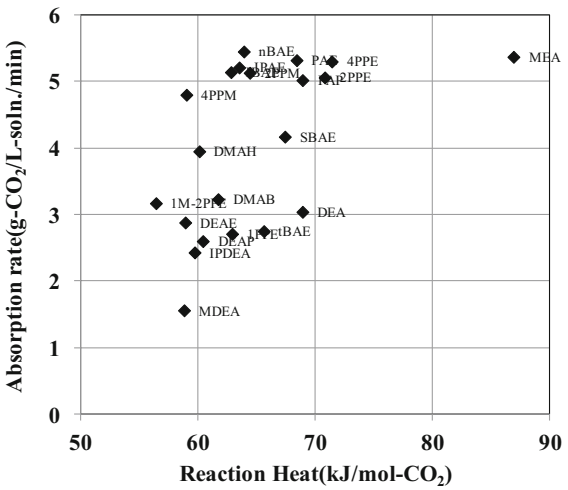

Fig. 9 Relationship between reaction heat and absorption rate[16]

Table 2 Prerequisites for estimation

Items	Units	Value
Capacity	Million tons/year	1
Plant operation rate	%	80
Absorbent s.w.	kg/m^3	1000
Diameter of absorption liquid	mm	0.5
Wall thickness	mm	10
Annual burden ratio	%	13

The cyclic capacity of secondary amines compared with MEA is high because CO_2 absorption results in the formation of bicarbonate anions. The cyclic capacities of 2-(isopropylamino)ethanol (IPAE), 2-(tert-butylamino)ethanol (tBAE), and (sec-butylamino)ethanol (SBAE) solutions were larger than for other secondary amine solutions. The three tertiary amines—4-(dimethylamino)butanol (DMAB), 6-(dimethylamino)hexanol (DMAH), and 1-methyl-2-piperidinemethanol (1 M-2PPM)—showed excellent absorption rates compared to MDEA.

The low absorption rate of *N*-isopropyldiethanolamine (IPDEA) may be attributed to the presence of two hydroxyl groups. Alcohol groups in the molecular structure tend to reduce the basicity of amines, while alkane groups tend to increase basicity. Screening results provided clear trends concerning the structural effects of hindered amine absorbents. Among secondary amines, the n-propyl, n-butyl, isopropyl, isobutyl, and 2- and 4-substituted piperidine rings were found to be the most suitable substituted functional groups for enhancing the absorption rate, and the isopropyl, tert-butyl, and sec-butyl groups were most suitable for enhancing cyclic capacity. For tertiary amines, the methyl and ethyl groups were found to be the most suitable substituted functional groups for enhancing the absorption rate.

Table 3 shows that the heat of reaction for all secondary amino alcohols is much lower than for conventional MEA absorbent. Among secondary absorbents, the two piperidine derivatives—2-piperidineethanol (2PPE) and 4-piperidineethanol (4PPE)—showed slightly higher reaction heats. All of the measured tertiary amines had similar reaction heats as MDEA except for synthetic 1 M-2PPE,

Table 3 Experimental results for screening and heat of reaction tests [15]

	Absorbent	Type[a]/hindered	Absorption rate	Absorption amount	Cyclic capacity	Cyclic cap. ratio = Cyclic capacity/absorption amount	Reaction heat
			$gCO_2/L/min$	gCO_2/L	gCO_2/L		$KJ/molCO_2$
1	PAE	s/	5.32	84	14	0.17	68.4
2	PAP	s/	5.02	86	18	0.21	68.9
3	BAE	s/	5.45	75	13	0.17	63.9
4	IPAE	s/h	5.21	100	31	0.31	63.5
5	BAE	s/h	2.75	96	24	0.25	65.6
6	SBAE	s/h	4.17	90	24	0.27	67.4
7	IBAE	s/	5.14	71	15	0.21	62.8
8	2PPM	s/h	5.13	89	17	0.19	64.4
9	4PPM	s/	4.8	89	12	0.13	59
10	2PPE	s/h	5.06	89	13	0.15	70.8
11	4PPE	s/	5.3	82	9	0.11	71.4
12	DMAB	t/	3.23	93	34	0.37	61.7
13	DMAH	t/	3.95	79	29	0.37	60.1
14	DEAE	t/	2.88	92	34	0.37	58.9
15	DEAP	t/	2.6	89	25	0.28	60.4
16	IPDEA	s/h	2.43	60	26	0.43	59.7
17	1 M-2PPE	s/h	3.17	77	25	0.32	56.4
18	1PPE	t/	2.71	73	35	0.48	62.9
19	MEA	p/	5.37	115	10	0.09	86.9
20	DEA	s/	3.04	69	16	0.23	68.9
21	MDEA	t/	1.56	55	24	0.44	58.8

h hindered

[a] Type = p: primary/s: secondary/t: tertiary

which exhibited a lower reaction heat. Figure 9 shows a comparison of the relationship between the heat of reaction and CO_2 absorption rates for conventional amines and the specific absorbents in this study. There was a trade-off between the heat of reaction and absorption rate for primary, secondary, and tertiary amines. That is, absorbents with greater absorption rate values tended to have greater heats of reaction with CO_2.

Further experimentation is required to characterize the new solvents with respect to their different properties. For example, rapid and economic synthesis was achieved with one pot–pot synthesis with high purity yield (>95 %), and high CO_2 screening (high absorption rate, high cyclic capacity, and low reaction heat) was achieved by tuning the particular chemical structures (e.g., aliphatic monoalkanolamines, aliphatic dialkanolamines, and cyclic alkanolamines, etc.) and alkyl substituents (e.g., methyl, propyl, isopropyl, isobutyl, secondary butyl, etc.) around the amino group. The hindered amine absorbents were synthesized by reacting alkylamine or alkanolamine with their corresponding chloroethanol or alkylhalide.

Sensible Heat

Cyclic capacities are important to calculate the sensible heat. However, from the viewpoint of experimental burden, the data for cyclic capacities (40–70 °C) is easy to obtain. Figure 10 shows the relationship between different cyclic capacities—(40–70 °C) and (40–120 °C).

The relationship is evident to a certain degree, but is more conspicuous between the different cyclic capacity ratios—(40–70 °C) and (40–120 °C)—in Fig. 11.

Next, the relationship between the reaction heat and cyclic capacity ratio was examined, as shown in Fig. 12. Both factors exhibited a negative relationship. This means that improving the reaction heat brings about an improvement in the cyclic capacity ratio at the same time.

Absorption Rate

Figure 13 shows the relationship between the cyclic capacity ratio and absorption rate, and it can be seen that they are negatively correlated. This result corresponds to the negative relationship between the reaction heat and the

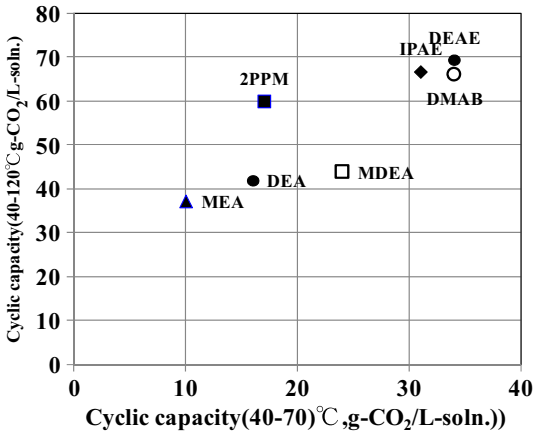

Fig. 10 Relationship between different cyclic capacities: (40–70 °C) and (40–120 °C)

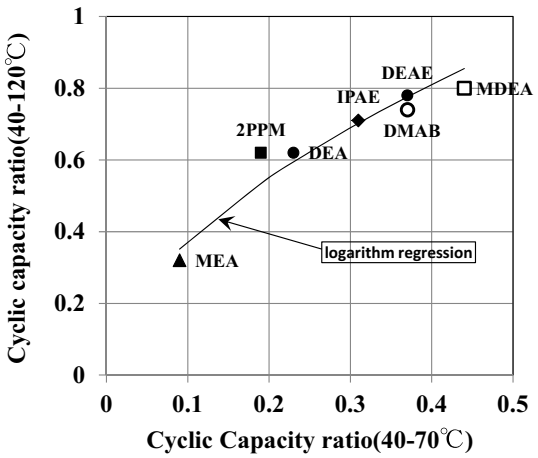

Fig. 11 Relationship between different cyclic capacity ratios: (40–70 °C) and (40–120 °C)

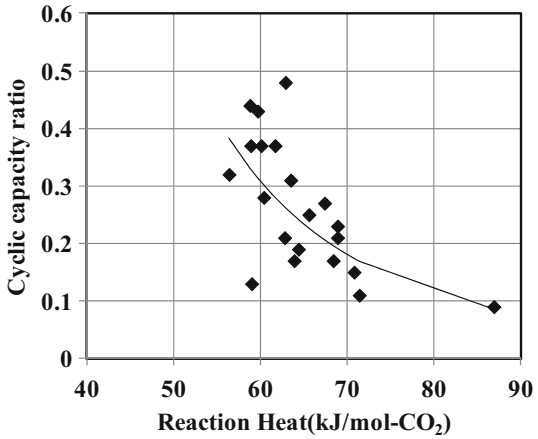

Fig. 12 Relationship between reaction heat and cyclic capacity ratio

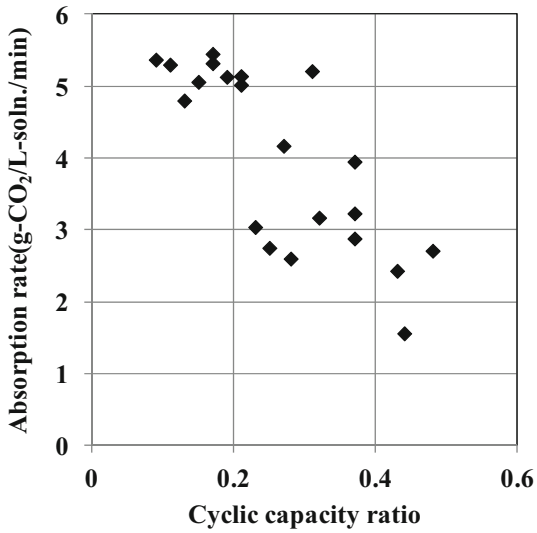

Fig. 13 Relationship between cyclic capacity ratio and absorption rate

absorption ratio, and is the reason why the cost estimate took into account both the reaction heat and absorption rate.

Discussion

We developed a chemical absorption method that successfully reduced the thermal energy consumption for CO_2 separation from 4 GJ/t-CO_2 to 2 GJ/t-CO_2 by using a high-performance absorbent and improving the chemical absorption process as shown in Fig. 9. Two pilot test plants were used to develop the process. The first was CAT1, which had a capacity of 1 ton of CO_2/day. This plant was used to evaluate the fundamental performance of the absorbent. The second plant was CAT30, which had a capacity of 30 tons of CO_2/day, and it was used to extensively evaluate the absorbent selected following testing in CAT1. In addition to the low energy consumption, the new absorbent has another unique and favorable feature. It easily releases CO_2 at a lower temperature than that of the conventional process for regeneration. This means that it may be possible to utilize waste low temperature heat at low cost.

Figure 14 shows the results of the relationship between the absorption rate and estimated facility cost. Using these results, Fig. 15 shows the influence of the reaction heat and absorption rate on the fixed (equipment cost only) and variable (energy cost only) relative costs. Generally, the reaction heat had a larger influence than the absorption rate. However, quantitatively, the absorption rate is also important as a secondary factor, and consequently, the total fixed and variable costs were reduced by 50 % compared to

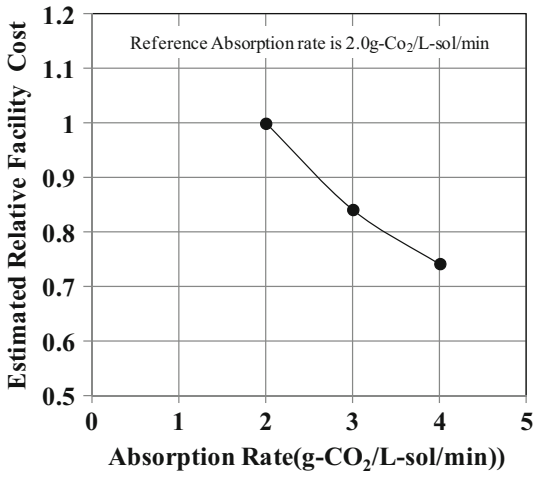

Fig. 14 Effect of absorption rate on estimated facility cost

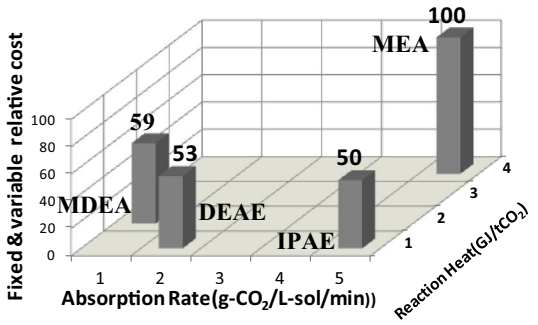

Fig. 15 Influence of reaction heat and absorption rate on fixed and variable relative costs

MEA. The fixed and variable relative costs were estimated based only on the reaction heat and absorption rate and do not include the influence of other factors related to each absorption liquid.

Conclusion

We developed a new technology in relation to the chemical absorption method as described above.

The COURSE50 project aims to develop new, drastic CO_2 reduction technologies. The final objective is to reduce CO_2 emissions from our steelworks by approximately 30 %. The project aims to achieve this reduction through an iron ore reduction achieved by using hydrogen-amplified coke oven gas to suppress CO_2 emissions from the blast furnace, as well as the separation and recovery of CO_2 from blast furnace gas using surplus exhaust heat in the steelworks. The goal of the project is to commercialize the first unit by around 2030 and then generalize the technologies by 2050 considering the timing of blast furnace equipment replacement.

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