

De-nitration Process in Glass Melter Off-Gas Treatment System—17092

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ABSTRACT

Vitrification technology has been generally applied to stabilize High-Level Radioactive Wastes (HLW) generated from spent fuel reprocessing for safe interim storage and final geological disposal. High temperature operation of the glass melter system generates substantial amounts of NO_x with various hazardous radioactive elements, due to HLW containing a lot of nitrate. Hence the off-gas treatment system (OGTS) is one of the essential systems for the removal of hazardous radioactive elements including NO_x, to ensure the stable and safe operation of the glass melter system.

In general, the wet scrubbing process (e.g. Sub-merged Bed Scrubber: SBS) is installed in the upstream of the OGTS for HLW vitrification in order to remove volatile ruthenium, cesium and other radioactive mists and dusts. NO_x together with ruthenium, iodine and submicron particles are removed in the wet absorber equipment to below the regulated limit by law. In the Rokkasho Vitrification Laboratory (RVL) constructed recently for inactive full scale mock-up tests, we have adopted the de-nitration process using reduction catalyst in addition to together with the wet scrubbing process considering the future scenarios that are compliant to the even stricter Air Pollution Control Law. By introducing this new system, we have successfully demonstrated a good de-nitration performance in the full scale mock-up test of the glass melter system.

On the other hand, by using the wet scrubbing process, nitric acid would be generated by the absorption of NO_x on this recovery process and should be reworked or disposed of as secondary liquid wastes. This is one of the deciding factors for enlarging the facility and increasing construction cost. That is the reason why IHI has developed the OGTS omitting the wet scrubbing process.

In this paper, we have summarized the results on the de-nitration process of the OGTS in RVL and the progress of the optimizing de-nitration process for future reprocessing system applications.

INTRODUCTION

RVL which is owned by Japan Nuclear Fuel Ltd. (JNFL) is a research and development facility that simulates High Active Liquid Waste Vitrification Facility (HVF). In RVL, developmental tests to advance the glass melter system have been

carried out using simulated wastes (inactive).

High temperature operation of the glass melter system in RVL generates substantial amounts of NO_x, because simulated wastes contain a lot of nitrate. In order to protect the environment around RVL, we had adopted the de-nitration process using a reduction catalyst in RVL.

In general, with the exception of nuclear reprocessing plant, alkaline scrubbers are adopted for OGTS of the glass melter, so as to remove hazardous elements according to their characteristics. On the other hand, RVL has the wet absorber equipment and HEPA filter as shown in Fig.1.

It is said that the de-nitration process using reduction catalyst is not suitable for the off-gas conditions which consists of many dusts and high concentration of NO_x. Therefore we have placed de-nitration using reduction catalyst downstream to the OGTS equipment.

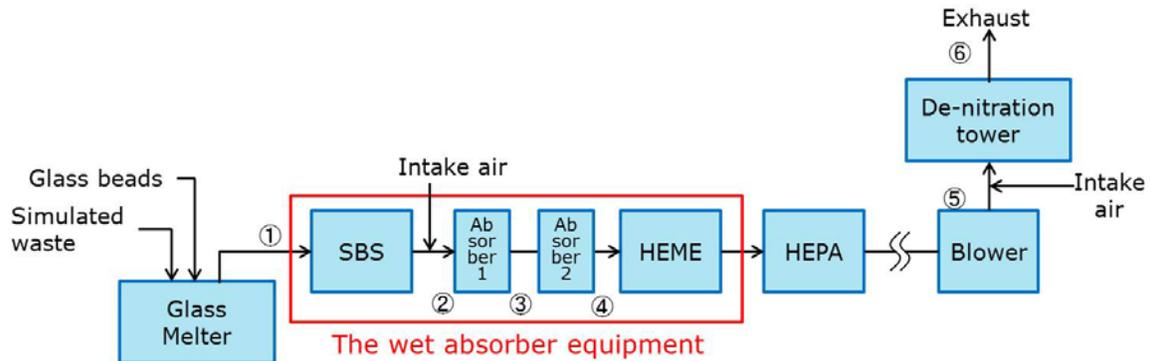


Fig.1. Process Flow of the OGTS in RVL

With attention paid to NO_x composition in design condition of RVL, we were already aware of the fact that the NO₂ ratio in NO_x from the RVL (same as HVF) is higher than the off-gas of furnace in other industries. However, in this case, there was insufficient knowledge in approximating the de-nitration performance using reduction catalyst.

We carried out the performance tests of the reduction catalyst which is selected by our pre-study on design conditions of RVL. We recognized that the performance of the de-nitration using the reduction catalyst is adapted to our requirement so we have decided the design of the de-nitration system for RVL.

RVL was completed in 2013 and various tests have been carried out for research and development there. In addition, we checked the de-nitration performance and the NO_x balances.

In this paper, we will mainly cover the results of de-nitration performance tests (laboratory scale test) and the operational results in RVL.

And furthermore, IHI has investigated dry type off-gas treatment system for future reprocessing system applications to reduce construction and operation costs. We will also touch on it in this paper.

DE-NITRATION PERFORMANCE TEST OF THE REDUCTION CATALYST (Laboratory Scale Test)

Comparison of the off-gas composition between RVL and the typical garbage incinerator is shown in TABLE 1.

TABLE 1 Comparison of the off-gas composition between RVL and garbage incinerator

	RVL	Garbage Incinerator
Off gas flow rate	3600Nm ³ /h	20000~70000Nm ³ /h
NO _x concentration	1200~5400ppm(*1)	About 150ppm
NO _x composition	NO ₂ :50~80%	NO ₂ :5%
Reduction Catalyst (*3)	TiO ₂ -V ₂ O ₅ -WO ₃ catalyst (*2)	TiO ₂ catalyst

(*1) design condition at de-nitration system inlet in RVL

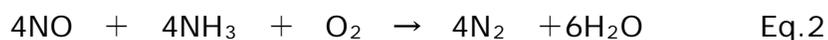
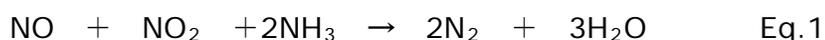
(*2) TiO₂ catalyst cannot treat off gas whose NO₂ is over 50%. Available catalyst is selected.

(*3) TiO₂-V₂O₅-WO₃ and TiO₂ belong to reduction catalyst.

In general, TiO₂ catalyst is widely adopted in many kinds of OGTS including garbage incinerators. However it is said that TiO₂-V₂O₅-WO₃ is more effective than TiO₂ catalyst for the off-gas whose NO₂ ratio in NO_x is above 50%. Therefore we selected TiO₂-V₂O₅-WO₃ for RVL.

However, shown above, there is insufficient data approximating the performance of de-nitration using reduction catalyst in the case that NO₂ ratio in NO_x is high so we carried out the laboratory scale test whose main parameters are NO and NO₂ comprised in NO_x.

We set the test conditions considering reaction equations on reduction catalyst (TiO₂-V₂O₅-WO₃) which are shown in the following:



We prepared the test equipment which can supply and measure NO and NO₂ separately while considering the equations above.

Test Equipment

Process flow of the test equipment is shown in Fig.2. The test equipment is composed of the following sections.

- "Gas Supply Section" composed of various gas cylinders and Mass Flow Meter (MFC).
- "Reaction Section" which has column filled with the reduction catalyst.
- "Measurement Section" which measure NO_x concentration of the gas after passing through the reaction section.
- "Off-Gas Treatment Section" which have alkali trap.

The NO_x is measured separately into total NO_x and NO by the NO_x analyzer via the chemiluminescent method. NO is automatically calculated by NO_x and NO measurement value in the analyzer.

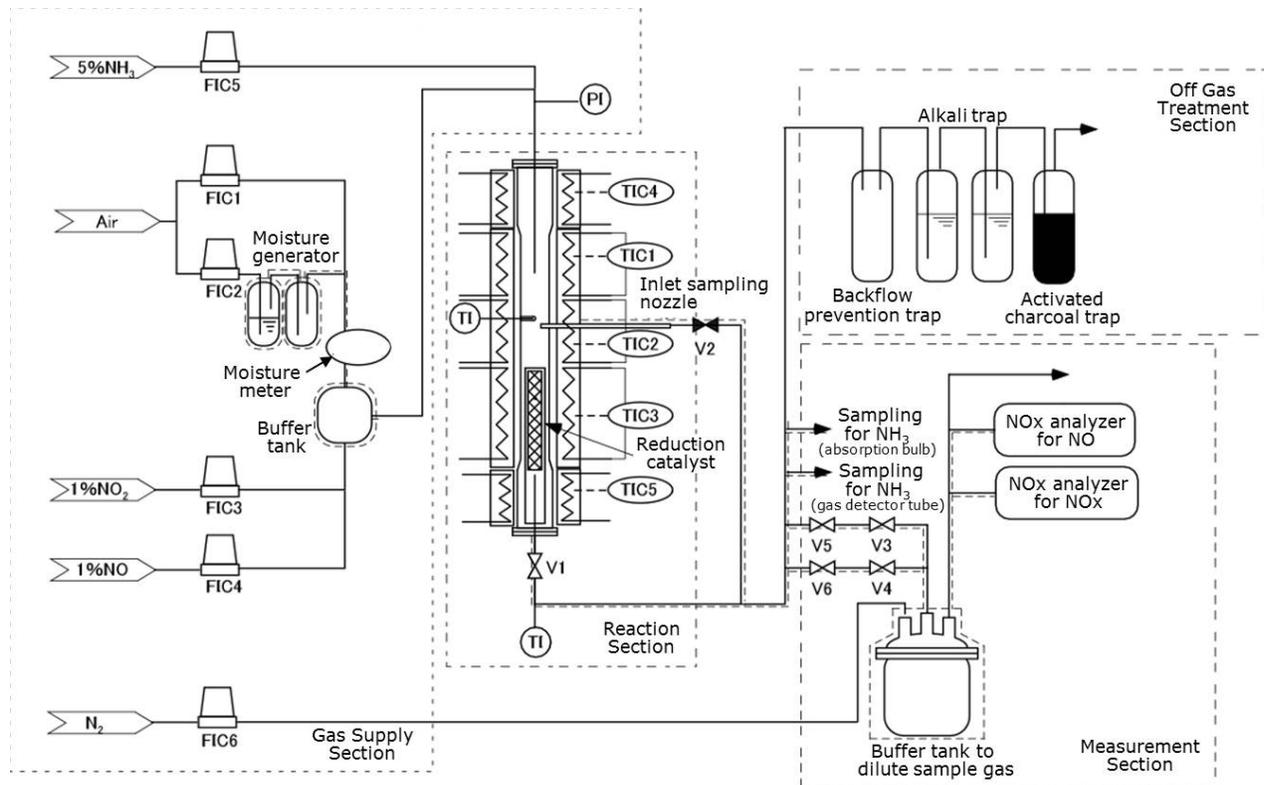


Fig.2. Process Flow of Test Equipment

Test Procedure

Test procedure is shown in the following.

- Reaction section heater is switched on.
- Supply specified amount of NO and NO₂ from each cylinder.
- Check that the NO_x concentration is at the specified value at de-nitration catalyst inlet by NO_x analyzer.
- Supply specified amount of 25% ammonia water. (De-nitration reaction starts by this operation)
- Measure NO_x concentration by NO_x analyzer.
- Measure NH₃ concentration by batch sampling at de-nitration catalyst outlet.
- Calculate removal efficiency of NO_x from outlet NO_x concentration including initial inlet NO_x concentration.
- After each test, supply hot air to accelerate the separation of NO_x from the catalyst.

Test Parameters

For test conditions we set the off-gas flow rate at 1 Nm³/h, because the test equipment is scaled down considering that off-gas flow rate of the design condition for RVL is 3600 Nm³/h. The off-gas flow rate is constant (1Nm³/h) and the parameters are shown as follows:

- Inlet NO_x concentration
- NO_x composition (NO₂ and NO ratio)
- Space velocity (SV) which is the off-gas flow rate divided by catalyst volume.

Test conditions are shown in TABLE 2.

TABLE 2 Test Conditions

Case		1	2	3	4	5	6	7
Off gas flow rate	Nm ³ /h	1	1	1	1	1	1	1
Inlet NOx concentration	ppm	100	100	100	600	1200	1200	5400
NOx composition	(NO ₂ /NO)	80/20	50/50	20/80	80/20	80/20	80/20	80/20
Inlet NH ₃ concentration	ppm	117	108	98	700	1400	1400	6300
SV	hr ⁻¹	4400	4400	4400	4400	4400	3300	3300
Temperature	°C	260	260	260	260	260	260	260

The required amount of NH₃ is calculated by reaction equations above and we set the amount of NH₃ to 92% of calculation results in each case. Because we verified amount of NH₃ based on the requirement of removal efficiency of NOx

SV is equal to the off-gas flow rate divided by catalyst volume. Small SV values lead to larger reduction catalyst volume. Therefore, the test can be safely evaluated by setting SV of the test condition larger than design condition.

Results and Discussions

Influence of NOx composition

We confirmed the influence of NOx composition on the removal efficiency of NOx. The results are shown in Fig.3. Inlet NOx concentration condition is constant (100ppm) as shown in TABLE 2.

In Case 2 which shows NO₂ ratio in NOx is 50%, the removal efficiency is highest. However, in Case1 which shows NO₂ ratio in NOx is 80%, the removal efficiency is lowest. In this case there is a considerable difference between the removal efficiency of NOx, NO₂ and NO.

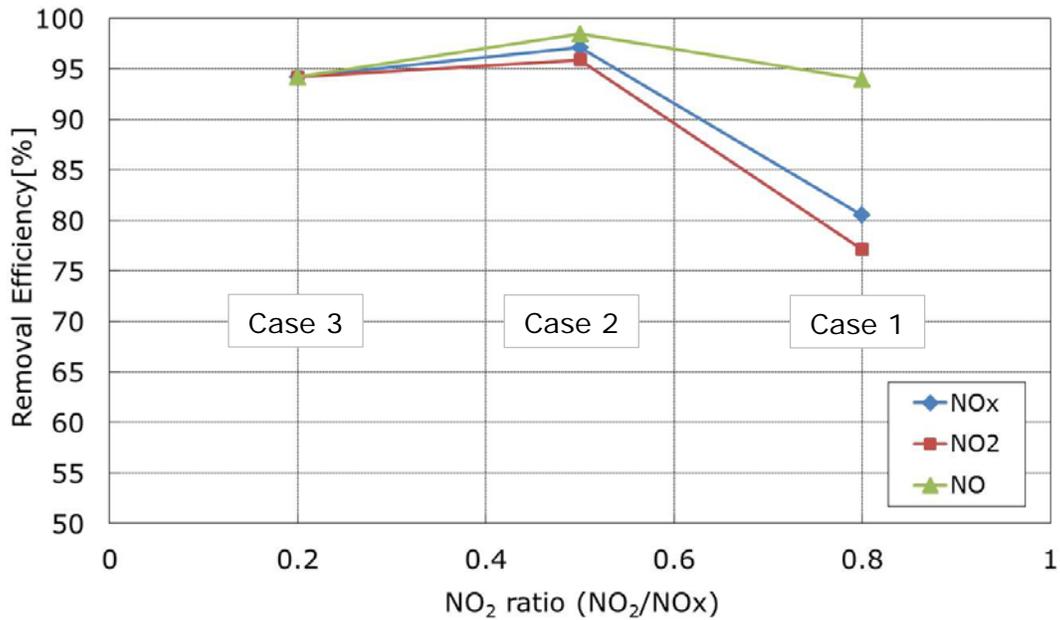


Fig.3. The Removal Efficiency of NO_x (the influence of NO_x composition)

Influence of NO_x Concentration and Catalyst Volume

We have studied the influence of NO_x concentration and SV on removal efficiency of NO_x, over the passage of time. The results are shown in Fig.4. It is shown that the removal efficiency of NO_x increases with the NO_x concentration. Furthermore, we found that the removal efficiency had a correlation to the passage of time, which showed saturation.

Gas conditions were the same for Case 5 and Case 6, but they differed in SV. From the comparison of these results in Fig.4, it was shown that the removal efficiency of NO_x increased by approximately 2% when the reduction catalyst volumes were increase by approximately 30%.

Case 4 to 7 showed the same NO_x composition but differed in SV. In contrast, there were slight differences in the saturated NO_x removal efficiency. This shows that the final removal efficiency of NO_x is almost the same when NO_x concentration was different, although the required time between start-up till saturated removal efficiency depends on NO_x concentration. We were able to confirm that the final removal efficiency is above 90% with the exception of Case 1.

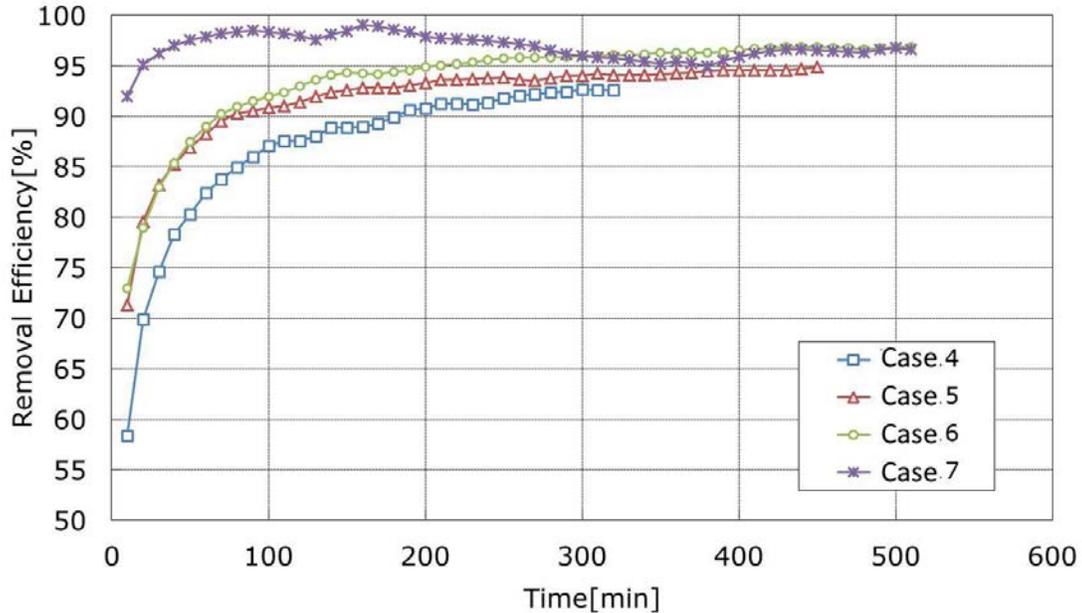


Fig.4 The Change of Removal Efficiency of NO_x with Passage of Time
(The influence of NO_x composition)

Conclusions of De-nitration Performance Test

From these tests we have learned the following:

- De-nitration is feasible in conditions where NO₂ ratio in NO_x is high.
- When the ratio of 'NO₂ and NO in NO_x' is 50:50, the removal efficiency was highest.
- If the NO_x concentration changes, the final removal efficiency differs slightly.
- In conditions where SV is less than 3300[hr-1], the removal efficiency is expected to be above 90%.

THE OPERATION RESULTS OF DE-NITRATION SYSTEM IN RVL

Considering the results above, we adopted the de-nitration system using the TiO₂-V₂O₅-WO₃ catalyst into RVL.

It is said that highly concentrated NO_x has a negative impact upon the catalyst because the de-nitration reaction by reduction catalyst is exothermic. The catalyst maker has recommended inlet NO_x concentration be set to 1200ppm. However, as shown in TABLE 1, NO_x concentration of design conditions for RVL is between 1200ppm to 5400ppm and it exceeds recommended value. Therefore we have optimized the system by adding intake air, in order to adhere to the maker's

recommendation of 1200ppm.

Urea and ammonia are generally known as the reductants for catalyst de-nitration. We selected 25% ammonia water to avoid the risk of having urea clogging at spray nozzle. 25% ammonia water is supplied to the evaporator by spray nozzle. After the ammonia water is vaporized and superheated in the evaporator, the ammonia gas of 260 °C is supplied to de-nitration system. The process flow of the de-nitration system in RLV is shown here in Fig.5.

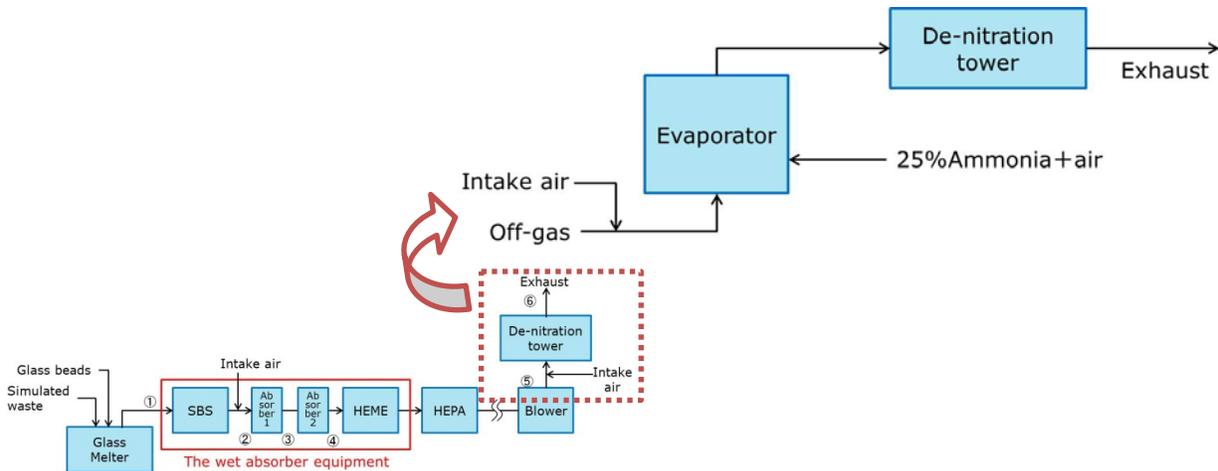


Fig.5. Concept of the De-nitration System in RVL

Samples of the off-gas and the liquid wastes can be easily taken from RVL, because it is a facility that treats only inactive materials. Therefore we took samples of the off-gas and evaluated the NO_x balances at the point shown in Fig.1 and at the following points as well:

- ① SBS inlet: Samples were not taken at this point. The amount of NO_x at this point depends on nitrate concentration and feeding rate of simulated wastes. We have supposed that all of nitrate contained in simulated waste would be transferred to the off-gas as NO_x.
- ② Absorber 1 inlet: we analyzed the NO_x balances by taking samples at this point once per batch.
- ③ Absorber 2 inlet : same as ②.
- ④ HEME inlet : same as ②.
- ⑤ De-nitration tower inlet: The NO_x balances are evaluated based on the analysis value by a permanently continuous analyzer.
- ⑥ De-nitration tower outlet: same as ⑤.

The NOx balances which are evaluated by the measurement results at each point are shown in TABLE 3.

TABLE 3 The NOx balances (In optimum condition)

		①	②	③	④	⑤	⑥
		SBS	Absorber 1	Absorber 2	HEME	De-nitration tower	
		Simulated waste (NO ₃ ⁻)	Inlet	Inlet	Inlet	Inlet	Outlet
Method		Calculation	Analysis (batch)	Analysis (batch)	Analysis (batch)	Analysis (continuous)	Analysis (continuous)
Off-gas flow rate	[Nm ³ /h]	276	650	650	650	3600	3600
NOx	[ppm]	18000	4300	2400	1800	300~400	0~1
NO	[mol/h]	-	92	43	30	30	~0
NO ₂	[mol/h]	-	33	27	22	22	~0
NOx	[mol/h]	225	125	69	52	52	~0
NO ₂ /NOx*100	[%]	-	26	39	42	42	-

Supposed NOx concentration from RVL is approximately 18000 ppm and they are partially removed by Absorber 1 and 2. As a result, NOx concentration in the De-nitration tower inlet ⑤ has been reduced to between 300 ppm to 400 ppm which is a 77% decrease. At the De-nitration tower outlet ⑥, given the optimum conditions, NOx can be reduced to near 0 ppm. This shows that the de-nitration system in RVL was able to decrease emissions of NOx under the detected limit of measurement.

Furthermore, it was found that NO₂ ratio in NOx is between 26% and 42% in RVL which was lower than our initial estimates under design conditions. However NO₂ ratio in NOx from RVL is still higher than other industries including a general garbage incinerator.

Considering the results above, we evaluated the NOx balances of the entire OGTS in RVL. The results are shown in TABLE 4.

TABLE 4 The NOx balances in the OGTS of RVL (In optimum condition)

		Simulated waste (NO ₃ ⁻)	The wet equipment						Reduction catalyst	
			SBS		Absorber 1		Absorber 2		De-nitration tower	
			Inlet	Outlet	Inlet	Outlet	Inlet	Outlet	Inlet	Outlet
NO	[mol/h]	-	-	92	92	43	43	30	30	~0
NO ₂	[mol/h]	-	-	33	33	27	27	22	22	~0
NOx	[mol/h]	225	225	125	125	69	69	52	52	~0
Amount of removal NOx	[mol/h]	-	100		56		17		52	
			173						52	
Removal rate of NOx	[%]	-	44		25		8		23	
			77						23	

Regarding the amount of NO_x, it was showed that 173 mol/h is removed by the wet absorber equipment and the remaining NO_x (52 mol/h) is removed by de-nitration system. NO_x removed by the wet absorber equipment is treated as liquid wastes and disposed as an industrial waste. In optimum condition, NO_x has been completely removed. Each of the removal rates of NO_x at the wet absorber equipment and the de-nitration system is shown in the following:

- The removal rate by the wet absorber equipment : approximately 77%
- The removal rate by the de-nitration system : approximately 23%

It has been proven that using the wet absorber equipment and reduction catalyst de-nitration system in RVL yields good results

In the future, we'll continue to observe the amount of NO_x from RVL to consider the operational life of the reduction catalyst and rational SV (the amount of the catalyst) for RVL.

INTRODUCTION OF PROGRESS WITH DE-NITRATION SYSTEM BY IHI

As shown above, the combined system of wet absorber equipment and de-nitration system produced good results for removing NO_x. However, approximately 77% of NO_x is absorbed by the wet absorber equipment. So they need to be reprocessed or disposed of as secondary liquid wastes.

Therefore IHI is investigating to modification the de-nitration system which meets future cost and performance requirements by omitting wet absorber equipment. IHI introduce the design concept in Fig.6 and the following:

- Reduce the load on the catalyst de-nitration by optimizing non-catalyst de-nitration system which supplies urea or ammonia directly to the glass melter.
- Keeping the temperature above the dew point of the off-gas to prevent condensation.
- Reprocess the condensed water generated from the off-gas to the glass melter in order to treat the secondary wastes within a self-sufficient system.

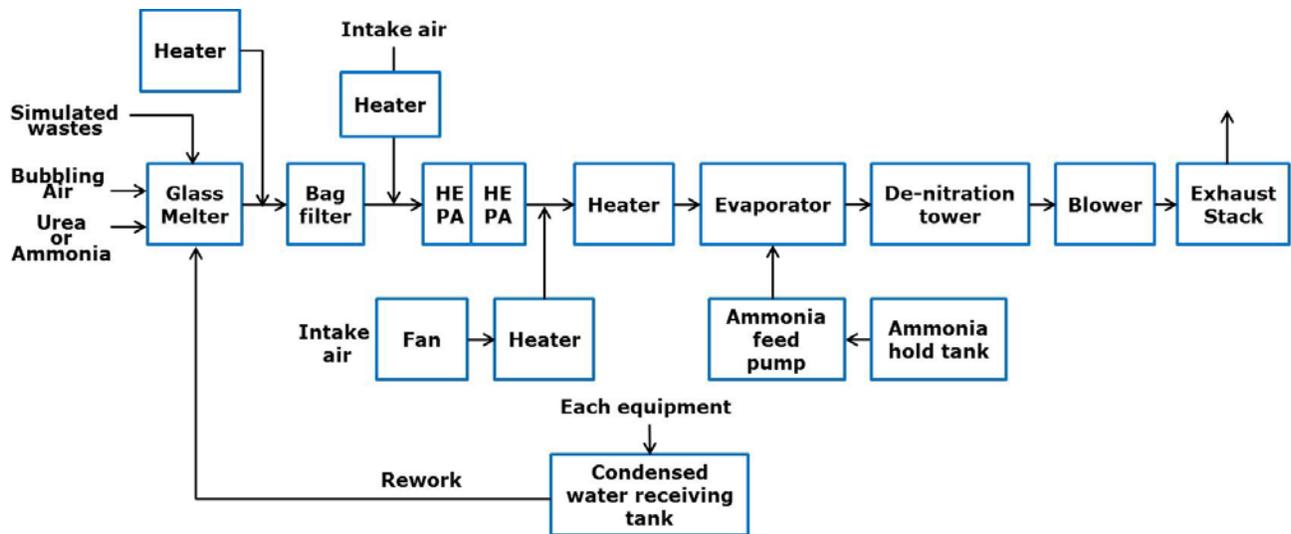


Fig.6. Design Concept of the OGTS omitting Wet Absorber Equipment

In this consideration, there are some problems we have identified as shown in the following:

- Confirm the feasibility of the non-catalyst de-nitration system in the glass melter.
- Establish on operation method to prevent clogging of dust generated from the glass melter at the pipes and dry decontamination equipment.
- Forecast the amount of condensed water generated in the OGTS.

In order to solve these problems and develop this design concept into the design of prototype system, we will execute the following plan:

- Consider in detail the optimum temperature for the OGTS.
- Consider how the condensed water affects the operation of the glass melter.
- Optimize the process design academically.
- Carry out the small scale mock-up tests to confirm the feasibility of a non-catalyst de-nitration system in the glass melter.

CONCLUSIONS

We carried out the de-nitration performance tests (laboratory scale tests) to check the removal efficiency of NO_x for the de-nitration system using a reduction catalyst (TiO₂-V₂O₅-WO₃) in which there was a high NO₂ ratio in NO_x. As a result, we have recognized that the performance of de-nitration using reduction catalyst meets requirements.

We adopted the de-nitration system using reduction catalyst (TiO₂-V₂O₅-WO₃) into RVL. At full scale mock-up tests for the glass melter in RVL, We have confirmed that NO_x has been completely removed in optimum conditions despite high NO₂ ratio in NO_x and approximately 77% of NO_x is absorbed by the wet absorber equipment.

We also introduced the progress of our research and development for OGTS omitting wet absorber equipment to reduce secondary waste. Now there are some problems we have identified, so we will continue to analyze the OGTS in detail in order to design more rational system.

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