

The Production of the Isotope ^{15}N by Isotopic Exchange in Nitrox System at Pressure

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The operation of ^{15}N production plant at pressure of 0.7 +/- 0.05 bar in stable conditions at total reflux and in production is demonstrated. The 10M HNO_3 flows used in the primary column were 6.6 L/h and 6.0 L/h, 47, respectively 33% higher than that of atmospheric pressure (4.5 L/h) and corresponding flow rates of the same column were 3.12 mL/cm².min, respectively 2.83 mL/cm².min for operation at pressure, compared to 2.12 mL/cm².min at atmospheric pressure. The 10M HNO_3 flows used in the final column were 324 mL/h and 264 mL/h, 62, respectively 32 % higher than that of the atmospheric pressure (200 mL/h) and flow rates of that column were: 3.05 mL/cm².min, respectively 2.49 mL/cm².min, compared to 1.86 mL/cm².min for atmospheric pressure operation. The HETP values are lower for both separation columns operated at pressure and higher 10M HNO_3 flow rates, that being an argument in the favour of operation the ^{15}N production plant by isotopic exchange in Nitrox system at pressure. The nitrogen enriched in ^{15}N losses in the waste sulphuric acid, evacuated at the bottom of product refluxer stage II, were : 5.18 -10.58 ppm of feeding with 10M HNO_3 of the plant. Any losses of nitrogen enriched in ^{15}N represent an additional uncontrolled production, which diminishes the production of ^{15}N plant. In the case of operation at pressure the flows of H^{15}NO_3 extracted as plant product are higher than those corresponding to atmospheric pressure because the nitric acid solution is chemically equilibrated with nitrogen oxides at the operation pressure and temperature. At a pressure of 1 atm. in the ^{15}N production plant the nitrogen content of nitric acid solution would be 10.919M instead of 10M.

Keywords: ^{15}N production, isotopic exchange, nitrox system, packed columns, pressure

The isotope ^{15}N , with a natural abundance of 0.365 at. %, has a cross section for neutron absorption of 8×10^{-5} barns, compared to the other stable isotope of nitrogen, ^{14}N , with a natural abundance of 99.635 at. %, which has a cross section for neutron absorption of 1.78 barns. According to that property the isotope ^{15}N is utilized in nuclear equipments, which cannot have natural abundance nitrogen in composition.

In nuclear energetics it is considered the utilization of nitride type nuclear fuels as U^{15}N , Pu^{15}N , etc., instead of oxidic fuels for generation IV nuclear reactors and Accelerator Driven Systems (ADS) for transmutation of the radioactive actinide of nuclear waste. It has to mention that for nitride fuel preparation it cannot use the most abundant nitrogen isotope, ^{14}N , because it gives radioactive ^{14}C and ^3H by participation to the reactions: $^{14}\text{N}(n,p)^{14}\text{C}$, $^{14}\text{N}(n,t)^{12}\text{C}$, [1 - 4]

Nitride type nuclear fuel has important advantages compared to oxidic fuel according its higher melting point, excellent thermal conductivity, higher fissile density, lower fission gas release and good radiation tolerance. For preparation of nitride nuclear fuel will be utilized the isotope ^{15}N at 99 at. % ^{15}N concentration, for the above mentioned reasons, but also to diminish the number of separation work unities (SWU) in the plant for ^{235}U enrichment for nuclear fuels.

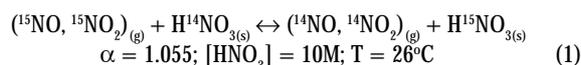
Taking into account that the world ^{15}N production is estimated at 20 - 40 Kg/year and the use of that isotope for production of nitride nuclear fuels for nuclear reactors and ADS, 1000 times increase of its production is estimated. In a 1000 TWhe nuclear park LWRs and fast neutron CAPRA reactors use oxidic fuels and ADS is assumed to operate on nitride fuel, where the nitrogen is enriched in ^{15}N . For that nuclear park 33.2 t/year of heavy metal needs to be fabricated into ADS fuel demanding 4.2 t of ^{15}N , which cost

is optimistic estimated at 50 million Euro/year (the price of ^{15}N 99 at. % was considered 10 Euro/g).

Implementation of ^{15}N recovery in the fuel reprocessing could decrease the penalty due to ^{15}N loss. The use of a closed gas cycle in the nuclear fuel fabrication stage is mandatory [5, 6].

Experimental part

The experimental test of ^{15}N separation by isotopic exchange in the system of nitrogen oxides in gaseous phase - 10M nitric acid solution, Nitrox system [7]:



at pressure was done on a cascade for production of ^{15}N with two columns connected in series. The primary column (P.C.) 730 cm length and 67 mm inside diameter, has a stainless steel packing of triangular wire springs 2.3x2.3x0.2 mm. The final column (F.C.) is 790 cm length and 15 mm inside diameter, with the same type packing, 1.8x1.8x0.2 mm.

After passing through the primary column the 10M HNO_3 solution arrives in the stage I of the product refluxer where it reacts with gaseous sulphur dioxide, fed at the bottom of it. The gaseous mixture of NO , NO_2 produced in stage I of the refluxer, enters in the stage II of the refluxer, fed with a supplementary flow of sulphur dioxide, so that the most important part of NO_2 is reduced to NO . The both stages of the product refluxer are Hastelloy C-276 made chemical reactors packed column type, resistant to the corrosion due to sulphuric acid, nitric acid, NO_x , and SO_2 . The refluxers were packed with 6x6 mm glass Raschig rings, chemical and thermic resistant. The refluxer of the final column [8] is a Hastelloy C-276 column type reactor,

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having an interior heat exchanger and a glass Raschig ring packing, 5x5 mm.

In all experiments presented in this paper the pressure of sulphur dioxide, feeding the plant refluxers, was 0.9 bar.

The sulphuric acid solution, produced in the refluxers of ^{15}N plant, is evacuated at the bottom of it. The sulphur dioxide flows were automatically controlled in order to maintain the reaction zone at constant height in the refluxer. If the reaction zone goes up to the top of the refluxer there is the possibility that sulphur dioxide enters in the isotope separation column damaging the stainless steel packing, by attack of sulphuric acid and sulphur dioxide.

If the reaction zone goes down to the refluxer bottom there is the possibility to loss nitrogen enriched in ^{15}N in the discarded sulphuric acid.

Results and discussions

A test of the final separation column included the following steps: the filling of the separation column with 10M HNO_3 solution to ensure a proper wetting of the packing, draining slowly the column with a flow of 10M HNO_3 , feeding with sulphur dioxide of the product refluxer. In table 1 is presented the results of 5 tests of the final column (F.C.), among them the run (2) has been done independently of the primary column (P.C.) and in the runs (3, 9, 11, 12) the final column was fed with 10M nitric acid extracted from the bottom of the primary column.

The flows utilized in the final column were 324 - 330 mL/h, the flow rates being: 3.056, respectively 3.11 mL/cm².min, 1.5 times higher than the flow rates used when the feeding sulphur dioxide pressure was lower. Table 1 does not include data on isotope separation, which was measured in the run (13) and the results will be presented later, in this paper. Except the run (13) in which the isotopic equilibrium of both separation columns was achieved, the other tests have been accomplished in 10 - 12 h, being experimentally followed: the fluids flowing, the automatic controlled feeding of sulphur dioxide, sulphuric acid evacuation at the bottom of the refluxers and the maintaining of the stable position of the HNO_3 - SO_2 reaction zone.

The test of the primary separation column (P.C.) were done in the same way as it was presented for the final column; that column has been fed with 10M nitric acid solution at 4.5 - 6.6 L/h., the flow rates being between 2.12 and 3.12 mL/cm².min (table 1). The flow rates increasing were possible according to the increasing of the sulphur dioxide pressure feeding the refluxers at 0.9 bar [9].

In the run (13) table 1, the variation of the ^{15}N separation in time, measured on the production plant, the SO_2 feeding pressure being 0.9 bar during 73 days of the experiment, has been determined. In the figure 1 are presented the isotopic equilibrium curves (isotope separation dynamics) of both columns of the plant. During run (13) the flows of 10M HNO_3 feeding the primary column were 6.6 L/h and 6.0 L/h and the flow rates of 3.12, respectively 2.83 mL/cm².min, compared to the flow 4.5 L/h and 2.12 mL/cm².min at lower pressure. In the run (13) the final column was fed with 10M HNO_3 , enriched in ^{15}N , from the bottom of the primary column, the flows being 324 mL/h, respectively 264 mL/h and flow rates 3.056 and respectively 2.49 mL/cm².min, compared to 200 mL/h and a flow rate of 1.88 mL/cm².min used at lower pressure.

After about 12 days of continuous operation the ^{15}N production was started with a 10M H^{15}NO_3 flow of 0.6 mL/h, the isotopic concentration at the bottom of final column being 99.6 at. % ^{15}N and 9.03 at. % ^{15}N , at the bottom of primary column. Actually the ^{15}N concentration at the bottom of the final column reached values higher than 99 at. % ^{15}N two days before, namely after about 10 days from the start of final column operation. The production flow was increased to 0.8 mL/h and then to 1.0 mL/h. On the graph of figure 1 are marked with horizontal lines the daily ^{15}N production levels of the plant during run (13). The vertical dashed line 1 marks the diminishing of the 10M HNO_3 flow of the final column from 324 to 264 mL/h and the dashed line 2 the diminishing of the 10M HNO_3 flow feeding the primary column from 6.6 to 6.0 L/h. The vertical dashed line 3 on the graph, (fig. 1), marks the increasing of the operation pressure in the separation plant to 0.7 +/- 0.05 bar, by partially closing of the valve on the line by which the gaseous mixture NO , NO_2 leaves the top of the primary column to nitric acid refluxer [7].

Because of the pressure variations on the SO_2 line, feeding product refluxers of the plant and the fact that the most part of SO_2 flow, entering in the stage I of the primary column refluxer was not automatically controlled, a cyclic changing of HNO_3 - SO_2 reaction zone position to the bottom, respectively to the top of the refluxer has been observed. In the first situation occurred losses of nitrogen enriched in ^{15}N in the waste sulphuric acid. In order to determine that losses the nitrogen from sulphuric acid was reduced to ammonia, which gives a yellow coloured compound by reaction with Nessler reagent, which was analysed by spectrophotometer at 425 nm. The nitrogen contents of 3 sulphuric samples were: 5.18, 6.71,

Table 1

EXPERIMENTAL DATA OF ^{15}N PRODUCTION PLANT. THE SO_2 FEEDING PRESSURE 0.9 BAR; P.C. = PRIMARY SEPARATION COLUMN; F.C. = FINAL SEPARATION COLUMN; I = 10M HNO_3 flow rate (mL/cm².min). *IN RUN (13) WERE ALSO UTILIZED THE FLOW 6.0 L/h IN P.C., RESPECTIVELY 264 mL/h IN F.C

Run Nr.	Flow 10M HNO_3 P.C. (L/h)	I P.C.	Flow 10M HNO_3 F.C. (mL/h)	I F.C.	Flow SO_2 P.C. Refluxer Stage I (L/h)	Flow SO_2 P.C. Refluxer Stage II (L/h)	Flow SO_2 F.C. Refluxer (L/h)
2	-	-	330	3.11	-	-	~93
3	4.5	2.12	327	3.08	1000	-	~108
4	4.5	2.12	-	-	1000	-	-
5	4.5	2.12	-	-	900	280	-
6	4.5	2.12	-	-	900	257	-
7	6.0	2.83	-	-	1200	336	-
8	6.6	3.12	-	-	1400	414	-
9	6.6	3.12	327	3.08	1400	396	~85
10	6.6	3.12	-	-	1400	420	-
11	6.6	3.12	327	3.08	1300	336	~101
12	6.6	3.12	324	3.05	1200	384	~101
13*	6.6	3.12	324	3.05	1200	384	~101

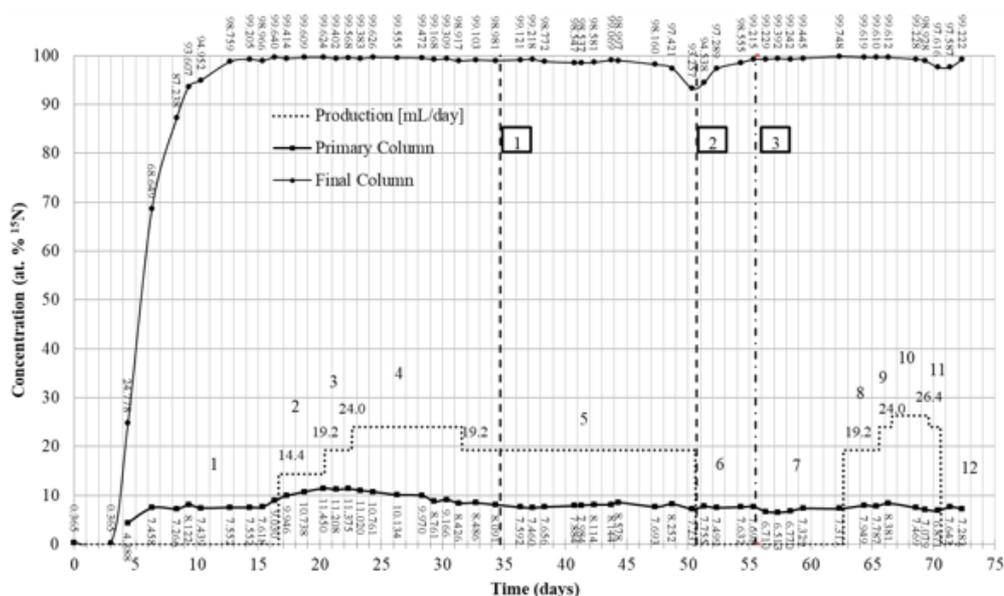


Fig. 1 Isotopic equilibration curves of the primary and final separation columns. The SO_2 feeding pressure 0.9 bar. [1] The final column flow has been changed from 324 to 264 mL/h; [2] The primary column flow rate has been changed from 6.6 L/h to 6.0 L/h; [3] The plant operation pressure has been increased from atmospheric to 0.7 +/- 0.05 bar; (1 - 12) number of the plateau on the separation curve

respectively 10.53 ppm of the 10M HNO_3 flow, feeding the ^{15}N separation plant.

The diminishing of the ^{15}N concentration (plateau 5, graph, fig. 1) is due to the improperly working of the stage I of the refluxer, which determined losses of nitrogen enriched in ^{15}N in the waste sulphuric acid.

The operation of the separation plant at 0.7 +/- 0.05 bar was tested. A stable operation of the ^{15}N separation plant at total reflux (plateau 7) and in production (plateau 8 - 11) has been observed. In table 2 are presented the experimental data obtained in 73 days of operation of ^{15}N separation plant.

The calculus of the isotopic separation (S) and of the height equivalent to theoretical plate (HETP) [10] for each column was done by using the mean values of the ^{15}N concentration of the plateaus 1 - 12, marked on the graph of figure 1. The HETP values were calculated not only in the case of operation at total reflux but also in production, in order to have comparison elements with the data of separation plant operated at atmospheric pressure, (table 3). It has to mention that in the case of operation at pressure the flows of H^{15}NO_3 , extracted as plant production, are higher than those corresponding to atmospheric pressure because the nitric acid solution is chemically equilibrated

with nitrogen oxides at the operation pressure and temperature. For instance if 10M HNO_3 solution is equilibrated with nitrogen oxides at 1 atm. and 30°C, the liquid phase composition is: $[\text{HNO}_3] = 5.21\text{M}$; $[\text{NO}_3] = 4.23\text{M}$; $[\text{N}_2\text{O}_4] = 0.43\text{M}$; $[\text{NO}_2] = 0.221\text{M}$; $[\text{N}_2\text{O}_3] = 0.091\text{M}$; $[\text{HNO}_2] = 0.198\text{M}$ thus the total nitrogen concentration of the liquid phase will be 10.919M [11]. In this situation, if the flow of H^{15}NO_3 extraction is 1 mL/h, at 1 atm. pressure it corresponds to 1.0919 mL/h.

The HETP values of both columns are lower in the case of operation at pressure (plateaus 8 -10, fig. 1) or actually at atmospheric pressure (plateaus 1-6, fig. 1) in both situation being used 10M HNO_3 flows (flow rates) 33, respectively 47% higher than those presented in table 3 for atmospheric pressure. The fact that have been used higher flows (flow rates) in the ^{15}N separation columns and HETP values are lower, than those determined at atmospheric pressure, represents an important argument in the favour of plant operation at pressure.

The mean production flow in the case of the three production periods at atmospheric pressure presented in table 3 has been 0.697 mL/h 10M H^{15}NO_3 , at a mean isotopic concentration of 92.85 at. % ^{15}N .

Table 2

EXPERIMENTAL DATA OF RUN (13); THE SO_2 FEEDING PRESSURE 0.9 BAR; I = 10M HNO_3 FLOW RATE (mL/cm².min); S = ISOTOPIC SEPARATION; HETP = HEIGHT EQUIVALENT TO THEORETICAL PLATE

Run Nr.	Flow 10M HNO_3 P.C. (L/h)	I P.C.	Flow 10M HNO_3 F.C. (mL/h)	I F.C.	Flow SO_2 P.C. Refluxer Stage I (L/h)	Flow SO_2 P.C. Refluxer Stage II (L/h)	Flow SO_2 F.C. Refluxer (L/h)
2	-	-	330	3.11	-	-	~93
3	4.5	2.12	327	3.08	1000	-	~108
4	4.5	2.12	-	-	1000	-	-
5	4.5	2.12	-	-	900	280	-
6	4.5	2.12	-	-	900	257	-
7	6.0	2.83	-	-	1200	336	-
8	6.6	3.12	-	-	1400	414	-
9	6.6	3.12	327	3.08	1400	396	~85
10	6.6	3.12	-	-	1400	420	-
11	6.6	3.12	327	3.08	1300	336	~101
12	6.6	3.12	324	3.05	1200	384	~101
13*	6.6	3.12	324	3.05	1200	384	~101

Table 3

EXPERIMENTAL DATA OF THE ¹⁵N PRODUCTION PLANT OPERATED AT ATMOSPHERIC PRESSURE; I = 10M HNO₃ FLOW RATE (mL/cm².min); S = ISOTOPIC SEPARATION: HETP = HEIGHT EQUIVALENT TO THEORETICAL PLATE: *TOTAL REFLEX: **PRODUCTION.

Flow 10M HNO ₃ P.C. (L/h)	I P.C.	Flow 10M HNO ₃ F.C. (mL/h)	I F.C.	S P.C.	HETP P.C. (cm)	S F.C.	HETP F.C. (cm)	Press. (bar)	Product. 10M H ¹⁵ NO ₃ (mL/h)	Plateau number (Graph Fig. 1)
6.6	3.12	324	3.05	22.19	12.60	1460	5.83	atm.*	0	1
6.6	3.12	324	3.05	31.31	11.34	1924	5.39	atm.	0.6	2
6.6	3.12	324	3.05	34.74	11.01	1313	5.89	atm.	0.8	3
6.6	3.12	324	3.05	29.48	11.55	1491	5.78	atm.	1.0	4
6.6	3.12	324/264	3.05/2.49	23.53	12.37	1281	5.91	atm.	0.8	5
6.0	2.83	264	2.49	22.59	12.53	452	6.92	atm.	0	6
6.0	2.83	264	2.49	20.31	12.97	2267	5.47	0.7	0	7
6.0	2.83	264	2.49	23.31	12.41	3022	5.28	0.7	0.8	8

In the case of operation of ¹⁵N plant at pressure a production flow of 0.9 mL/h of 10M H¹⁵NO₃ at 99 at. % ¹⁵N would be 27 % higher than that achieved at atmospheric pressure. That increasing is considered important taking into account that it was achieved on the same plant, without any additional energy consumption, because the plant pressure will be increased based only on the liquid sulphur dioxide vapour pressure of the cylinder.

Conclusions

The operation of ¹⁵N production plant (two separation columns connected in series) at pressure of 0.7 +/- 0.05 bar in stable conditions at total reflux and in production is demonstrated.

10M HNO₃ flows used in the primary column were 6.6 L/h and 6.0 L/h, 47, respectively 33% higher than that of atmospheric pressure (4.5 L/h).

The flow rates of the primary column were 3.12 mL/cm².min, respectively 2.83 mL/cm².min for operation at pressure, compared to 2.12 mL/cm².min at atmospheric pressure.

10M HNO₃ flows used in the final column were 324 mL/h and 264 mL/h, 62, respectively 32 % higher than that of the atmospheric pressure (200 mL/h).

The flow rates of the final column were: 3.05 mL/cm².min, respectively 2.49 mL/cm².min, compared to 1.86 mL/cm².min for atmospheric pressure operation.

HETP values are lower for both separation columns operated at pressure and higher 10M HNO₃ flow rates, that being an argument in the favour of operation the ¹⁵N production plant by isotopic exchange in Nitrox system at pressure.

The nitrogen enriched in ¹⁵N losses in the waste sulphuric acid, evacuated at the bottom of product refluxer stage II, were : 5.18 - 10.58 ppm of feeding with 10M HNO₃ of the plant. Any losses of nitrogen enriched in ¹⁵N represent an additional uncontrolled production, which diminishes the production of ¹⁵N plant.

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