

# Coupled Mass–Energy Assessment of Process-Air Redistribution in A Medium-Pressure Nitric Acid Plant

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**Abstract:** This paper quantifies the first-principles production and heat-recovery potential of redistributing process air in a medium-pressure AK-72M weak-nitric-acid unit. The assessed concept replaces part of the T-5–K-47 heating/bleaching branch with an external air stream and redirects an equal amount of already-compressed M-10A air to the R-12/1,2 contact reactors. A stoichiometric oxygen balance, an effective overall yield factor and a reaction-heat model were evaluated for 2,500–10,000 Nm<sup>3</sup> h<sup>−1</sup>. At the documented effective oxygen basis of 19 vol.% and  $\eta_{\text{tot}} = 0.955\text{--}0.965$ , the 10,000 Nm<sup>3</sup> h<sup>−1</sup> scenario gives 2.552–2.578 t h<sup>−1</sup> of additional 100% HNO<sub>3</sub> equivalent, 4.477–4.523 t h<sup>−1</sup> of 57 wt.% solution and 20.21–20.42 kt y<sup>−1</sup> of HNO<sub>3</sub> equivalent at 7,920 h y<sup>−1</sup>. Using 20.95 vol.% as a dry-air boundary increases the calculated production range to 2.814–2.843 t h<sup>−1</sup>, demonstrating that oxygen basis and humidity must be measured rather than assumed. Gross additional steam potential is 2.55–2.87 t h<sup>−1</sup> for the 19% basis and 80–90% heat recovery, but this is not a net utility benefit because the reduced T-5 duty may increase T-202 steam demand. The study defines the measurements and equipment constraints required to convert the model-based potential into a validated industrial result.

**Keywords:** Nitric acid; Ostwald process; mass balance; heat recovery; process air; oxygen basis; industrial validation; AK-72M.

## Highlights

A coupled oxygen, product and reaction-heat model is developed for process-air redistribution.

At 10,000 Nm<sup>3</sup> h<sup>−1</sup> and 19% O<sub>2</sub>, predicted additional HNO<sub>3</sub> is 2.552–2.578 t h<sup>−1</sup>.

Changing the oxygen basis from 19.0% to 20.95% raises the estimate by approximately 10.3%.

The 2.55–2.87 t h<sup>−1</sup> steam result is a gross potential, not a verified net saving.

**1. Introduction:** The industrial Ostwald process couples catalytic oxidation of ammonia, oxidation of NO, reactive absorption of NO<sub>x</sub> and substantial heat recovery [3–6]. The main oxidation step is highly exothermic, while absorber performance depends on

pressure, temperature, oxygen availability and gas–liquid contact [8,9]. Turbomachinery and heat exchangers connect these chemical operations through gas flow, shaft power and steam. Consequently, an apparent increase in oxygen feed can be limited by reactor velocity, boiler duty, compressor maps, absorber hydraulics or tail-gas treatment.

In the AK-72M case, M-10A supplies 162,800–202,400  $\text{Nm}^3 \text{h}^{-1}$  to the R-12/1,2 contact reactors and 17,000–35,000  $\text{Nm}^3 \text{h}^{-1}$  to the T-5–K-47 heating/bleaching branch [1,2]. The evaluated concept supplies external air to replace part of the second branch and reallocates an equal amount of M-10A air to the contact section. It therefore seeks additional reaction capacity without a

large increase in total M-10A flow. Because the K-47 branch also transfers heat in T-5, product and energy consequences must be evaluated together.

The contribution of this work is a transparent boundary calculation that separates: (i) the documented effective oxygen basis from the standard dry-air boundary; (ii) 100%  $\text{HNO}_3$  equivalent from 57 wt.% product solution; (iii) gross reaction-heat recovery from net plant utility benefit; and (iv) model potential from industrial validation. The model is intended for research screening and does not define operating setpoints or retrofit construction details.

## 2. System boundary and calculation method

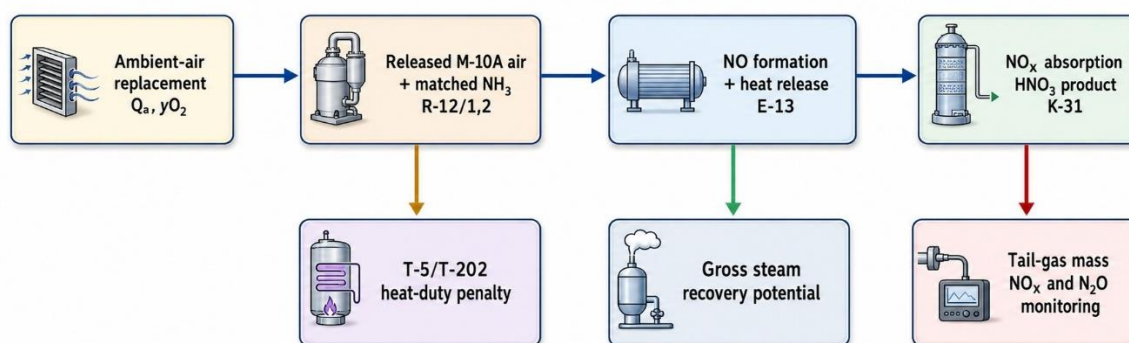


Figure 1. Coupled mass–energy boundary for evaluating the redistribution concept.

### 2.1. Basis and assumptions

Table 1. Calculation basis and quantities requiring industrial confirmation.

| Quantity                                     | Value used                                                | Status                                            |
|----------------------------------------------|-----------------------------------------------------------|---------------------------------------------------|
| External-air scenarios, $Q_a$                | 2,500; 5,000; 7,500; 10,000 $\text{Nm}^3 \text{h}^{-1}$   | Model inputs                                      |
| Oxygen volume fraction, $y_{\text{O}_2}$     | 0.190 documented effective basis; 0.2095 dry-air boundary | Measure composition and humidity                  |
| Effective overall yield, $\eta_{\text{tot}}$ | 0.955–0.965                                               | Separate conversion and absorption in later model |
| Product concentration                        | 57 wt.% $\text{HNO}_3$                                    | Verify laboratory product analysis                |
| Annual operating time                        | 7,920 $\text{h y}^{-1}$                                   | Equivalent to 330 $\text{d y}^{-1}$               |
| Heat-recovery efficiency, $\eta_{\text{HR}}$ | 0.80–0.90                                                 | Replace with E-13 plant heat balance              |
| Normal-volume convention                     | 273.15 K, 101.325 kPa (calculation basis)                 | Confirm plant reporting convention                |

The 19% oxygen value is retained because the supplied concept document associated 1,900 Nm<sup>3</sup> h<sup>-1</sup> O<sub>2</sub> with 10,000 Nm<sup>3</sup> h<sup>-1</sup> external air. It is lower than the 20.95% oxygen fraction of dry atmospheric air. The difference may reflect a wet or process-specific reporting basis, measurement uncertainty or an unrecorded dilution. Both cases are therefore reported explicitly instead of silently substituting one for the other.

## 2.2. Product and ammonia balances

For a first plant-wide stoichiometric approximation, the net relation  $\text{NH}_3 + 2\text{O}_2 \rightarrow \text{HNO}_3 + \text{H}_2\text{O}$  is used. It represents the combined oxidation and absorption chain, not the elementary reaction over the gauze. With a normal molar gas volume  $V_m = 22.4 \text{ Nm}^3 \text{ kmol}^{-1}$ , the theoretical and effective HNO<sub>3</sub> rates are:

$$G_{\text{HNO}_3, \text{th}} = \frac{Q_a O_2 M_{\text{HNO}_3}}{2V_m} \quad (1)$$

$$G_{\text{HNO}_3} = G_{\text{HNO}_3, \text{th}} M \eta_{\text{tot}} \quad (2)$$

$$G_{\text{HNO}_3, \text{eq}} = \frac{Q_a y_{\text{O}_2} M_{\text{NH}_3}}{2V_m} \quad (3)$$

where  $M_{(\text{HNO}_3)} = 63 \text{ kg kmol}^{-1}$  and  $M_{(\text{NH}_3)} = 17 \text{ kg kmol}^{-1}$ .  $\eta_{\text{tot}}$  is an effective product-yield factor that combines contact conversion, selectivity and absorption into one screening parameter. A future validated model should estimate these contributions separately and close balances for NH<sub>3</sub>, O<sub>2</sub>, N<sub>2</sub>, H<sub>2</sub>O, NO, NO<sub>2</sub>, N<sub>2</sub>O and HNO<sub>3</sub>.

An independent mixing check is also required because

the R-12 feed is specified at 9.2–10.6 vol.% NH<sub>3</sub>. For a given incremental contact-air flow  $V_{\text{air}}$ , the ammonia volume required to preserve a selected fraction  $x_{\text{NH}_3}$  is  $V_{\text{NH}_3} = x_{\text{NH}_3} V_{\text{air}} / (1 - x_{\text{NH}_3})$ . This check is not equivalent to the net oxygen balance because oxygen also supports downstream NO oxidation and residual O<sub>2</sub> leaves the absorber.

## 2.3. Heat-recovery model

The supplied regulation reports 907.3 kJ per 4 mol NH<sub>3</sub> for the principal oxidation reaction. Gross additional reaction heat and recoverable steam are estimated from:

$$Q_{\text{rxn}} = n_{\text{NH}_3, \text{conv}} \frac{907.3}{4} \quad (4)$$

$$D_{\text{steam}} = \frac{Q_{\text{rxn}} \cdot \eta_{\text{HR}}}{i_{\text{steam}} - i_{\text{fw}}} \quad (5)$$

where  $\eta_{\text{HR}}$  is varied from 0.80 to 0.90 and the steam/feedwater enthalpy difference is represented by the plant screening basis used in the source calculation.  $D_{\text{steam}}$  is a gross heat-recovery potential. Net steam benefit additionally subtracts any increase in T-202 heating demand and includes changes in pumps, compressors, expanders and mechanical losses.

## 3. RESULTS

### 3.1. Additional nitric-acid potential

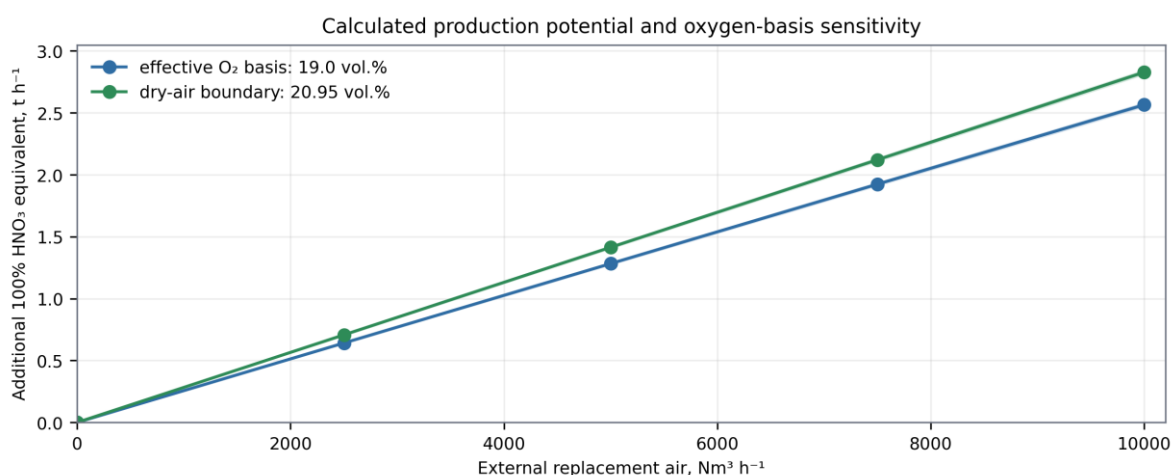


Figure 2. Additional 100% HNO<sub>3</sub>-equivalent production under two oxygen bases; bands show  $\eta_{\text{tot}} = 0.955$ –0.965.

**Table 2. Product scenarios for the documented effective oxygen basis ( $y_{O_2} = 0.190$ ).**

| $Q_a$ , $Nm^3 h^{-1}$ | 100% $HNO_3$ , $t h^{-1}$ | 57% solution, $t h^{-1}$ | Annual $HNO_3$ , $kt y^{-1}$ |
|-----------------------|---------------------------|--------------------------|------------------------------|
| 2,500                 | 0.638–0.645               | 1.119–1.131              | 5.05–5.11                    |
| 5,000                 | 1.276–1.289               | 2.238–2.262              | 10.10–10.21                  |
| 7,500                 | 1.914–1.934               | 3.357–3.393              | 15.16–15.32                  |
| 10,000                | 2.552–2.578               | 4.477–4.523              | 20.21–20.42                  |

The response is linear because oxygen fraction and  $\eta_{tot}$  are constant within each scenario. At 10,000  $Nm^3 h^{-1}$ , the calculation gives 2.552–2.578  $t h^{-1}$  of 100%  $HNO_3$  equivalent. Dividing by 0.57 gives 4.477–4.523  $t h^{-1}$  of 57 wt.% product solution. Reporting these two

quantities separately prevents the common error of comparing an acid-equivalent mass with a solution mass.

**Table 3. Oxygen-basis sensitivity at  $Q_a = 10,000 Nm^3 h^{-1}$ .**

| $y_{O_2}$ | $O_2$ , $Nm^3 h^{-1}$ | 100% $HNO_3$ , $t h^{-1}$ | 57% solution, $t h^{-1}$ | Annual $HNO_3$ , $kt y^{-1}$ |
|-----------|-----------------------|---------------------------|--------------------------|------------------------------|
| 0.1900    | 1,900                 | 2.552–2.578               | 4.477–4.523              | 20.21–20.42                  |
| 0.2095    | 2,095                 | 2.814–2.843               | 4.936–4.988              | 22.28–22.52                  |

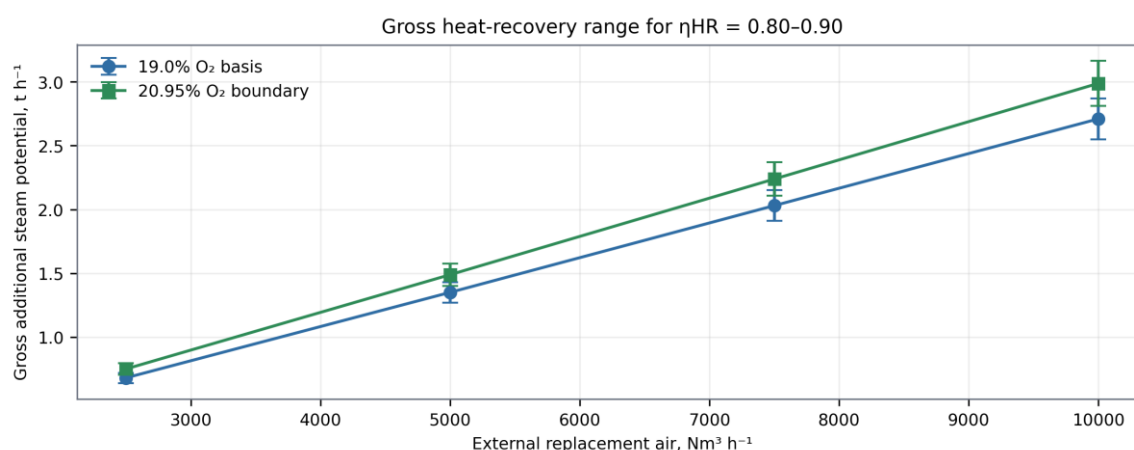
Changing only the oxygen basis from 19.0% to 20.95% increases the result by 10.26%. This difference is larger than the 1.05% span caused by  $\eta_{tot} = 0.955$ –0.965. Oxygen analysis, humidity correction and a clear normal-volume convention are therefore primary data-quality requirements.

### 3.2. Ammonia–air consistency check

For 10,000  $Nm^3 h^{-1}$  of incremental contact air, holding  $NH_3$  at 9.2, 10.0 and 10.6 vol.% requires approximately 1,013, 1,111 and 1,186  $Nm^3 h^{-1}$   $NH_3$ , respectively, or about 0.770–0.901  $t h^{-1}$  on the normal-volume basis.

The net oxygen balance gives an  $NH_3$  equivalent of about 0.721  $t h^{-1}$  at  $y_{O_2} = 0.19$ . The mismatch is expected because the mixing constraint and the plant-wide oxygen balance answer different questions. Final ammonia demand must be obtained from a component balance spanning the contact-reactor inlet through the absorber outlet, including residual oxygen and side-product selectivity.

### 3.3. Gross steam potential and net-energy qualification



**Figure 3. Gross steam-recovery potential; error bars represent  $\eta_{HR} = 0.80\text{--}0.90$ .****Table 4. Gross steam potential for  $y_{O_2} = 0.190$ .**

| $Q_a$ , $\text{Nm}^3 \text{h}^{-1}$ | $Q_{rxn}$ , $\text{Gcal h}^{-1}$ | Steam at $\eta_{HR} 0.80\text{--}0.90$ , $\text{t h}^{-1}$ | Theoretical upper bound, $\text{t h}^{-1}$ |
|-------------------------------------|----------------------------------|------------------------------------------------------------|--------------------------------------------|
| 2,500                               | 0.551                            | 0.64–0.72                                                  | 0.80                                       |
| 5,000                               | 1.103                            | 1.27–1.43                                                  | 1.59                                       |
| 7,500                               | 1.654                            | 1.91–2.15                                                  | 2.39                                       |
| 10,000                              | 2.206                            | 2.55–2.87                                                  | 3.18                                       |

At 10,000  $\text{Nm}^3 \text{h}^{-1}$ , the gross additional steam estimate is 2.55–2.87  $\text{t h}^{-1}$  on the 19% oxygen basis. A value near 3.18  $\text{t h}^{-1}$  corresponds to an idealized upper bound and should not be reported as an achieved utility saving. The external-air concept can reduce hot M-10A flow through T-5; if this increases T-202 steam demand, part of the E-13 gain is consumed internally. A defensible net result requires simultaneous measurement of E-13 steam production, T-202 steam use, feedwater conditions and the complete M-10 shaft power balance.

#### 4. Process-capacity and environmental constraints

Additional contact air raises total gas volume through R-12/1,2, E-13/1,2, K-27, M-10V, cooling equipment, K-31 and the tail-gas train. In turbulent sections, pressure loss is approximately proportional to the square of velocity; therefore, a modest flow increase can consume hydraulic margin rapidly [16–18]. Equipment-specific geometry and performance maps were not supplied, so no safe operating limit is inferred from the screening calculation.

Environmental performance must be expressed as mass per unit product, not concentration alone. For a measured tail-gas flow  $V_{tg}$  and concentration  $C_{NOx}$ , the  $\text{NO}_x$  mass flow should be calculated on a consistent dry/wet and reference-oxygen basis, then divided by 100%  $\text{HNO}_3$ -equivalent production.  $\text{N}_2\text{O}$  requires the same treatment because gauze selectivity can change with local flow and temperature [7,13–15]. Without measured tail-gas flow and composition, this paper makes no claim of  $\text{NO}_x$  or  $\text{N}_2\text{O}$  reduction.

#### 5. Limitations and industrial validation

The principal limitations are the absence of a time-resolved operating dataset; the uncertain oxygen and humidity basis; the use of one effective  $\eta_{tot}$

parameter; and missing geometry/performance maps for T-5, E-13, the M-10 train and K-31. Accordingly, the results are model-based potentials. A validation dataset should cover representative stable operation and include synchronized flow, pressure, temperature,  $\text{O}_2$ ,  $\text{NO}_x$ ,  $\text{N}_2\text{O}$ , product concentration, steam and shaft-power measurements with instrument uncertainty.

The model should be assessed with mass-balance closure, parity plots, RMSE, MAE, bias and uncertainty intervals. Any plant modification also requires qualified engineering design, process-hazard analysis, mechanical and hydraulic verification, protection logic and authorization by the responsible plant organization. The calculations are not an operating instruction.

#### 6. CONCLUSIONS

A transparent coupled model was developed to screen product and heat-recovery effects of reallocating M-10A process air from the T-5–K-47 branch to R-12/1,2.

For  $Q_a = 10,000 \text{ Nm}^3 \text{h}^{-1}$ ,  $y_{O_2} = 0.190$  and  $\eta_{tot} = 0.955\text{--}0.965$ , additional production is 2.552–2.578  $\text{t h}^{-1}$  of 100%  $\text{HNO}_3$  equivalent or 4.477–4.523  $\text{t h}^{-1}$  of 57 wt.% solution.

The dry-air boundary  $y_{O_2} = 0.2095$  raises the product estimate by 10.26%, making oxygen-basis verification more important than the narrow  $\eta_{tot}$  range used here.

Gross steam potential is 2.55–2.87  $\text{t h}^{-1}$  at the 10,000  $\text{Nm}^3 \text{h}^{-1}$  scenario, but net utility benefit remains unknown until T-5/T-202 duty and the complete shaft-power balance are closed.

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