

**STATE-OF-THE-ART  
FOR THE PRODUCTION OF NITRIC ACID  
WITH REGARD TO THE IPPC DIRECTIVE**

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MONOGRAPHIEN  
Band 150  
M-150

Wien, 2001

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**Cover**

Simplified schematic representation of a M/H dual pressure nitric acid plant

The Federal Environment Agency would like to thank Agrolinz Melamin GmbH for their excellent co-operation.

**Impressum**

Editor: Umweltbundesamt GmbH (Federal Environment Agency Ltd)  
Spittelauer Lände 5, A-1090 Wien (Vienna), Austria

Printed by: Riegelnik, A-1080 Wien

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ISBN 3-85457-612-9

## TABLE OF CONTENTS

	Page
<b>ZUSAMMENFASSUNG UND SCHLUSSFOLGERUNGEN</b> .....	7
<b>Ziel der Studie</b> .....	7
<b>Herstellung von Salpetersäure</b> .....	7
<b>Ausgangsmaterialien</b> .....	8
<b>Energie</b> .....	8
<b>NO<sub>x</sub>-Emissionen und Massnahmen zur Minderung von NO<sub>x</sub>-Emissionen</b> .....	8
Selektive katalytische Reduktion (SCR).....	8
Primäre Maßnahmen zur NO <sub>x</sub> Emissionsminderung – Verbesserte Absorption.....	11
Nicht selektive katalytische Reduktion (NSCR).....	11
<b>N<sub>2</sub>O-Emissionen und Massnahmen zur Minderung von N<sub>2</sub>O Emissionen</b> .....	11
<b>Abwasser</b> .....	13
<b>Abfälle und Reststoffe</b> .....	13
<b>Salpetersäureherstellung in Österreich</b> .....	13
<b>SUMMARY AND CONCLUSIONS</b> .....	14
<b>Object of the Study</b> .....	14
<b>Production of Nitric Acid</b> .....	14
<b>Starting Materials</b> .....	15
<b>Energy</b> .....	15
<b>NO<sub>x</sub> Emissions and Emission Reduction</b> .....	15
Selective Catalytic Reduction (SCR).....	15
Process Integrated Measures for NO <sub>x</sub> Emission Reduction – Measures for Achieving High Absorption Efficiencies.....	18
Non-selective Catalytic Reduction (NSCR).....	18
<b>N<sub>2</sub>O Emissions and Emission Reduction</b> .....	18
<b>Wastewaters</b> .....	20
<b>Wastes and Residues</b> .....	20
<b>Nitric Acid Production in Austria</b> .....	20
<b>1 INTRODUCTION</b> .....	21
<b>1.1 Object of the Study</b> .....	21
<b>1.2 Reference to the IPPC-Directive</b> .....	21
<b>1.3 Historical Aspects</b> .....	22
<b>1.4 Production and Use of Nitric Acid</b> .....	22
<b>1.5 Production and Consumption of Nitric Acid in Austria</b> .....	23

<b>2</b>	<b>TECHNOLOGY OF NITRIC ACID PRODUCTION</b> .....	24
<b>2.1</b>	<b>Input/Output</b> .....	25
2.1.1	Ammonia.....	25
2.1.2	Air.....	25
2.1.3	Water.....	25
2.1.4	Catalysts.....	26
<b>2.2</b>	<b>Products</b> .....	27
<b>2.3</b>	<b>Production of Weak Nitric Acid</b> .....	28
2.3.1	Catalytic Combustion of Ammonia.....	28
2.3.2	Oxidation and Absorption of Nitrogen Oxides.....	29
2.3.3	Process Technology of Weak Nitric Acid Production.....	30
2.3.3.1	Single Pressure Plants.....	30
2.3.3.2	Dual Pressure Plants.....	31
<b>2.4</b>	<b>Processes for the Production of Concentrated Nitric Acid</b> .....	33
<b>2.5</b>	<b>Energy</b> .....	33
<b>2.6</b>	<b>Storage</b> .....	35
<b>3</b>	<b>AIR EMISSIONS AND EMISSION REDUCTION</b> .....	36
<b>3.1</b>	<b>Emissions of Nitrogen Oxides (NO<sub>x</sub>)</b> .....	36
<b>3.2</b>	<b>Emissions of Nitrous Oxides (N<sub>2</sub>O)</b> .....	37
<b>3.3</b>	<b>Other Air Emissions</b> .....	39
3.3.1	Diffuse Emissions.....	39
3.3.2	Emissions from Start-up and Shut-down Operations.....	39
3.3.3	Secondary Emissions.....	39
<b>3.4</b>	<b>Reduction of NO<sub>x</sub> Emissions</b> .....	39
3.4.1	End-of-pipe Processes for the Reduction of NO <sub>x</sub> Emissions.....	39
3.4.1.1	Selective Catalytic Reduction (SCR Process).....	40
3.4.1.2	Non-Selective Catalytic Reduction (NSCR).....	47
3.4.2	End-of-pipe Processes Not or No Longer Applied for NO <sub>x</sub> Emission Reduction in Nitric Acid Plants.....	48
3.4.2.1	Selective Non-catalytic Abatement Techniques (SNCR).....	48
3.4.2.2	Adsorption Processes.....	48
3.4.2.3	Alkaline Final Absorption.....	48
3.4.3	Process Integrated Measures for the Reduction of NO <sub>x</sub> Emissions – Measures for Achieving High Absorption Efficiencies.....	49
3.4.3.1	Absorption Pressure.....	49
3.4.3.2	Absorption Temperature.....	50
3.4.3.3	Absorption Column Design.....	50
<b>3.5</b>	<b>Reduction of N<sub>2</sub>O Emissions</b> .....	51
3.5.1	Measures for the Reduction of N <sub>2</sub> O Formation – Primary Measures.....	53
3.5.1.1	Operating Conditions.....	53
3.5.1.2	Catalysts.....	53
3.5.2	Available Measures for the Reduction of N <sub>2</sub> O Emissions.....	53
3.5.2.1	Non-selective Catalytic Reduction (NSCR).....	53
3.5.2.2	Homogenous Decomposition in the Ammonia Combustion Unit.....	53

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3.5.3	Emerging Techniques for the Reduction of N <sub>2</sub> O Emissions .....	54
3.5.3.1	Modifications of the Catalyst for Ammonia Conversion .....	54
3.5.3.2	Catalytic Decomposition of N <sub>2</sub> O in the Ammonia Combustion Unit.....	54
3.5.3.3	Catalytic Decomposition/Reduction of N <sub>2</sub> O in the Tail Gas .....	55
<b>4</b>	<b>WASTEWATER</b> .....	<b>56</b>
4.1	Process Condensates .....	56
4.2	Periodic Blowdown .....	56
4.3	Diffuse Emissions .....	56
4.4	Cooling Water .....	56
<b>5</b>	<b>WASTES AND RESIDUES</b> .....	<b>57</b>
5.1	Filters .....	57
5.2	Waste Oils .....	57
5.3	Spent Catalysts.....	57
<b>6</b>	<b>NITRIC ACID PLANTS IN AUSTRIA</b> .....	<b>58</b>
<b>7</b>	<b>LEGISLATIVE REGULATIONS</b> .....	<b>59</b>
7.1	<b>Austria</b> .....	<b>59</b>
7.1.1	Emissions to Air .....	59
7.1.2	General Licensing Requirements .....	59
7.1.3	Ambient Air Concentration .....	59
7.1.4	Air Quality Management Plans.....	60
7.1.5	Wastewater Regulations .....	60
7.2	<b>Germany</b> .....	<b>61</b>
7.3	<b>Protocol to the 1979 Convention on Long-range Transboundary Air Pollution to Abate Acidification, Eutrophication and Ground-level Ozone</b> .....	<b>62</b>
<b>8</b>	<b>MONITORING OF EMISSIONS</b> .....	<b>63</b>
<b>9</b>	<b>REFERENCES</b> .....	<b>64</b>



## ZUSAMMENFASSUNG UND SCHLUSSFOLGERUNGEN

### Ziel der Studie

Ziel der Studie ist es, den Stand der Technik in der Herstellung von Salpetersäure im Hinblick auf die IPPC-Richtlinie zu beschreiben. Die Studie behandelt dabei angewandte Technologien, Einsatzstoffe und produktspezifische Emissionen (inkl. Abfälle und Reststoffe) bei der Salpetersäureherstellung. Ein wichtiges Anliegen der Studie ist das Aufzeigen von Minderungspotenzialen bei Luftschadstoffen. Primäre und sekundäre Maßnahmen zur Minderung von Luftemissionen werden beschrieben und Kosten für ausgewählte sekundäre Verfahren abgeschätzt. Die spezifische Situation in Österreich wird beschrieben.

### Herstellung von Salpetersäure

Die Herstellung von Salpetersäure erfolgt nach dem Ostwald Verfahren. Ammoniak wird an einem Edelmetallkatalysator zu NO oxidiert. NO wird weiter oxidiert und in Wasser absorbiert, wobei Salpetersäure gebildet wird.

**Schwachsäure** wird mit Konzentrationen bis zu 69,2 % hergestellt. Ein großer Teil der produzierten Salpetersäure wird für die Herstellung von mineralischen Düngemittel (NPK Dünger, Kalkammonsalpeter) verwendet. Schwachsäure wird auch für die Herstellung von Ammonnitrat sowie für die Adipinsäureherstellung (Ausgangsmaterial für die Nylon- und Polyesterproduktion) eingesetzt. Verfahrensweisen für die Herstellung von Schwachsäure unterscheiden sich in erster Linie in Hinblick auf die bei der katalytischen  $\text{NH}_3$ -Oxidation und bei der Absorption angewandten Drücke. Folgende Druckbereiche werden unterschieden:

- N: Normaldruck (nur für die katalytische  $\text{NH}_3$ -Oxidation angewandt);
- M: Mitteldruck (3–6 bar) and
- H: Hochdruck (> 8 bar).

Abbildung I zeigt eine vereinfachte schematische Darstellung der Schwachsäureherstellung. Prinzipiell werden zwei Verfahrensweisen unterschieden, Eindruck- und Zweidruckanlagen:

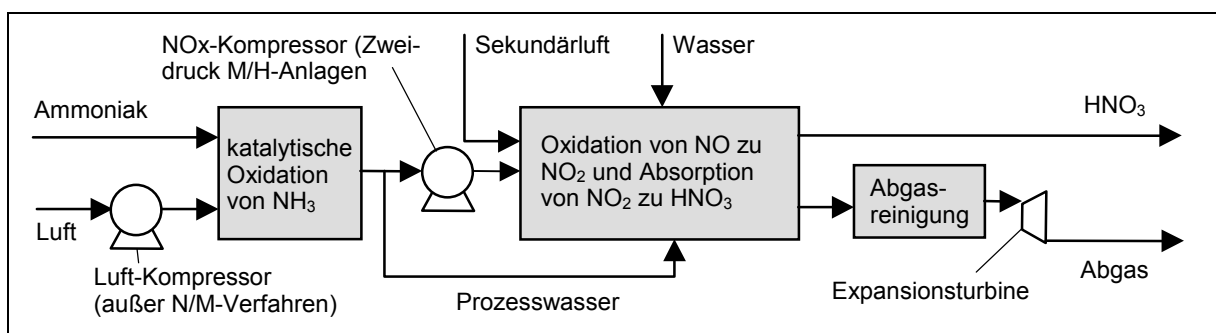


Abb. I: Vereinfachte schematische Darstellung der Herstellung von Salpetersäure (Schwachsäure)

Bei **Eindruckanlagen** erfolgt die katalytische Oxidation und die Absorption unter dem gleichen Druck. Es werden M/M-Anlagen (Mitteldruck für Oxidation und Absorption) und H/H-Anlagen (Hochdruck für Oxidation und Absorption) betrieben.

Bei **Zweidruckanlagen** erfolgt die katalytische Oxidation von Ammoniak bei geringerem Druck als die Absorption. Üblicherweise sind M/H-Anlagen (Mitteldruck für Oxidation und Hochdruck für Absorption) im Einsatz. Einige N/M-Altanlagen (Normaldruck für Oxidation und Mitteldruck für Absorption) sind ebenfalls noch im Einsatz.

Bei der Herstellung von Schwachsäure ist die Verfahrensweise ausschlaggebend für das Emissionsniveau und den Ressourcenverbrauch. Ein niedriger (bzw. mittlerer Druck) im Reaktor für die katalytische Oxidation von Ammoniak begünstigt die Umwandlung von  $\text{NH}_3$  zu  $\text{NO}$ , und ermöglicht eine höheren Ausbeute bzw. niedrigeren  $\text{N}_2\text{O}$  Emissionen. Hoher Druck in der Absorptionskolonne begünstigt die Absorption und führt ebenfalls zu höherer Ausbeute und niedrigeren  $\text{NO}_x$  Emissionen. Insgesamt können Zweidruckanlagen somit effizienter betrieben werden als Eindruckanlagen.

**Konzentrierte Salpetersäure** wird durch indirekte Verfahren (Aufkonzentrierung von Schwachsäure mit Hilfsstoffen) oder durch direkte Verfahren (Herstellung von flüssigem  $\text{N}_2\text{O}_4$ , welches unter Druck mit Sauerstoff und verdünnter Salpetersäure zu konzentrierter  $\text{HNO}_3$  reagiert) hergestellt. Die Herstellung von konzentrierter Salpetersäure ohne Hilfsstoffe durch direkte Destillation von Schwachsäure ist nicht möglich.

## Ausgangsmaterialien

Ausgangsmaterialien für die Herstellung von Salpetersäure sind Ammoniak (in Abhängigkeit der Verfahrensweise 280–290 kg  $\text{NH}_3$ /t  $\text{HNO}_3$ ), Wasser und Luft.

Erhebliche Verluste an eingesetzten Pt/Pd-Katalysatoren treten bei der katalytischen Oxidation von Ammoniak unter mittleren bzw. hohen Drücken auf. Edelmetalle werden mit unterhalb der Katalysatornetze installierten Rückgewinnungssystemen wiedergewonnen.

## Energie

Bei der Herstellung von Salpetersäure ist ein hohes Ausmaß an Energierückgewinnung Stand der Technik. Eine moderne Zweidruckanlage produziert etwa 11 GJ/t  $\text{HNO}_3$ -N als Hochdruckdampf, entsprechend etwa 2.4 GJ/t  $\text{HNO}_3$  (100 %ig).

## $\text{NO}_x$ -Emissionen und Massnahmen zur Minderung von $\text{NO}_x$ -Emissionen

Nach der Absorptionskolonne hängt die  $\text{NO}_x$ -Konzentration des Restgases vor allem vom Absorptionsdruck ab. Geringer  $\text{NO}_x$  Emissionsniveaus können durch eine optimierte Absorption (z.B. durch die Anwendung hoher Absorptionsdrücke) und/oder durch sekundäre Minderungsverfahren erreicht werden. Zur Reduktion von  $\text{NO}_x$ -Emissionen sind bei den meisten Salpetersäureanlagen sekundäre Minderungstechnologien installiert. Von diesen sekundären Minderungsverfahren entspricht das **SCR-Verfahren** (selektive katalytische Reduktion) dem **Stand der Technik für die Minderung von  $\text{NO}_x$  Emissionen**. Das NSCR-Verfahren (nicht-selektive katalytische Reduktion) entspricht nicht dem Stand der Technik, da dieses Verfahren Verlagerungseffekte (hohe Sekundäremissionen und hohen Brennstoffverbrauch) mit sich bringt. Auch nachgeschaltete alkalische Absorptionsverfahren sind nicht Stand der Technik. SNCR-Verfahren (Selektive nicht-katalytische Reduktion) werden aus energetischen Gründen bei Salpetersäureanlagen nicht eingesetzt.

### Selektive katalytische Reduktion (SCR)

Beim SCR-Verfahren reagiert  $\text{NO}_x$  an einem Katalysator selektiv mit Ammoniak, der als Reduktionsmittel zugegeben wird. Mit dem SCR-Verfahren sind bei Salpetersäureanlagen Minderungsraten von bis zu 95 % erreichbar. Das SCR-Verfahren ist bei Neu- und Altanlagen Stand der Technik. Bei Neuanlagen entspricht die Kombination von SCR mit einer Hochdruck-Absorptionskolonne (> 8 bar) dem Stand der Technik.



Mit einer derartigen Kombination eines **SCR-Verfahrens mit einer Hochdruck-Absorptionskolonne** (> 8 bar) sind Emissionen von **100–200 mg NO<sub>x</sub>/Nm<sup>3</sup>** (als NO<sub>2</sub>) erreichbar. Tabelle I zeigt eine Abschätzung der wesentlichen Kosten für eine Nachrüstung eines SCR Reaktors bei einer bestehenden M/H Salpetersäureanlage.

Tab. I: *Wesentliche Kosten für eine Nachrüstung eines SCR Reaktors in einer bestehenden M/H-Zweidruckanlage; die Kosten wurden für eine Produktion von 900 t HNO<sub>3</sub>/Tag, einen Abgasvolumenstrom von 110.000 Nm<sup>3</sup>/h, einer NO<sub>x</sub> Reduktion von 0,3 g NO<sub>x</sub>/Nm<sup>3</sup> (als NO<sub>2</sub>) und einer Rohgaskonzentration von < 200 mg NO<sub>x</sub>/Nm<sup>3</sup> (als NO<sub>2</sub>) abgeschätzt.*

		€/Einheit	€/a
<b>Betriebsbedingungen:</b>			
Abgasvolumenstrom [Nm <sup>3</sup> /h]	110.000		
Betriebsstunden [h/a]	8.400		
NO <sub>x</sub> Rohgaskonzentration [mg/Nm <sup>3</sup> als NO <sub>2</sub> ]	500		
NO <sub>x</sub> Reingaskonzentration [mg/Nm <sup>3</sup> als NO <sub>2</sub> ]	200		
<b>Investitionskosten exkl. Katalysator [€]</b>	<b>925.000</b>		
<b>Belastung aus den Investitionskosten inkl. Zinsen</b>			<b>95.400</b>
Anzahl der Jahre	15		
Zinssatz [%]	6		
<b>Wartung und Verschleiß:</b>			<b>18.500</b>
Wartung und Verschleiß [% der Investitionskosten]	2		
<b>Energiebedarf:</b>			
Arbeitsdruck (bar)	9		
Druckverlust des SCR Reaktors (mbar)	10		
Betriebstemperatur des SCR Reaktors (°C)	190		
<b>zusätzlicher Energiebedarf des Kompressors (wegen Druckverlust des SCR Reaktors) [kWh/h]</b> <sup>1)</sup>	8	0,044 €/kWh <sup>1)</sup>	<b>3.050</b> <sup>1)</sup>
<b>zusätzliche Energieverbraucher [kWh/h]</b> <sup>1)</sup>	10	0,044 €/kWh <sup>1)</sup>	<b>3.660</b> <sup>1)</sup>
<b>SCR Katalysator inkl. Zinsen (Zinssatz: 6 %)</b>			<b>8.300</b>
spezifische Katalysatorkosten [€/kg]		18 €/kg	
Menge des Katalysators [kg]	3.400		
durchschnittliche Lebensdauer des Katalysators [a]	10		
<b>flüssiger Ammoniak</b>			<b>35.500</b> <sup>2)</sup>
spezifische Kosten von fl. Ammoniak [€/t] <sup>2)</sup>	20		
Verbrauch an Ammoniak [kg/h]:		220 €/t <sup>2)</sup>	
<b>BEWERTETE JÄHRLICHE KOSTEN FÜR SCR [€/a]</b>			<b>164.400</b> <sup>2)</sup>
<b>SPEZIFISCHE MEHRKOSTEN BEZOGEN AUF DIE PRODUKTION [€/t HNO<sub>3</sub>]</b>			<b>0,55</b> <sup>2)</sup>
<b>SPEZIFISCHE MEHRKOSTEN BEZOGEN AUF DIE REDUKTION VON NO<sub>x</sub> [€/t NO<sub>x</sub>]</b>			<b>593</b> <sup>2)</sup>

<sup>1)</sup> Spezifische Kosten für elektrische Energie wurden vom Umweltbundesamt auf Basis früherer Studien (vgl. WIESENBERGER & KIRCHER, 2001) mit 0,044 €/kWh angenommen.

<sup>2)</sup> Spezifische Kosten von flüssigem NH<sub>3</sub> wurden vom Umweltbundesamt auf Basis früherer Studien (vgl. EK-KER & WINTER, 2000) mit 220 €/t angenommen. In der Literatur sind spezifische Kosten von Ammoniak für die Emissionsminderung in HNO<sub>3</sub>-Anlagen im Bereich von 100 \$/t (SCHWEFER et al., 2000) und 200 €/t (POTTIER, 2001) angegeben. Die geringeren Kosten könnten möglicherweise darauf zurückgeführt werden, dass die Verfügbarkeit von NH<sub>3</sub> am Standort berücksichtigt wurde. Berücksichtigt man die geringeren Kosten in der oben angeführten Abschätzung so vermindern sich die jeweiligen Kosten um etwa 15 %.

In Kombination mit einer **Mitteldruck-Absorptionskolonne** (4–8 bar) sind **mit dem SCR-Verfahren** Emissionen von **200–350 mg NO<sub>x</sub>/Nm<sup>3</sup>** (als NO<sub>2</sub>) erreichbar. Tabelle II zeigt eine Abschätzung der wesentlichen Kosten für die Installation eines SCR Verfahrens im Zuge einer Adaptierung einer alten Normaldruckanlage.

Tab. II: Wesentliche Kosten einer SCR Anlage, welche im Zuge einer Adaptierung einer alten Normaldruckanlage (Neubau einer Mitteldruck-Absorptionskolonne) installiert wurde; bei der Kostenabschätzung wurde von einer Produktion von 500 t/Tag, einem Abgasvolumenstrom von 65.000 Nm<sup>3</sup>/h, einer Rohgaskonzentration von 4.000–6.000 mg NO<sub>x</sub>/Nm<sup>3</sup> (als NO<sub>2</sub>) und einer Reingaskonzentration von < 350 mg NO<sub>x</sub>/Nm<sup>3</sup> (als NO<sub>2</sub>) ausgegangen.

		€/Einheit	€/a
<b>Betriebsbedingungen:</b>			
Abgasvolumenstrom [Nm <sup>3</sup> /h]	65.000		
Betriebsstunden [h/a]	8.400		
NO <sub>x</sub> Rohgaskonzentration [mg/Nm <sup>3</sup> als NO <sub>2</sub> ]	4.300		
NO <sub>x</sub> Reingaskonzentration [mg/Nm <sup>3</sup> als NO <sub>2</sub> ]	320		
<b>Investitionskosten exkl. Katalysator [€]</b>	<b>353.200</b>		
<b>Belastung aus den Investitionskosten inkl. Zinsen</b>			<b>36.400</b>
Anzahl der Jahre	15		
Zinssatz [%]	6		
<b>Wartung und Verschleiß:</b>			<b>7.060</b>
Wartung und Verschleiß [% der Investitionskosten]	2		
<b>Energiebedarf:</b>			
Arbeitsdruck (bar)	4,8		
Druckverlust des SCR Reaktors (mbar)	50		
Betriebstemperatur des SCR Reaktors (°C)	270		
<b>zusätzlicher Energiebedarf des Kompressors (wegen Druckverlust des SCR Reaktors) [kWh/h]</b> <sup>1)</sup>	54	0,044 €/kWh <sup>1)</sup>	<b>19.830</b> <sup>1)</sup>
<b>zusätzliche Energieverbraucher [kWh/h]</b> <sup>1)</sup>	10	0,044 €/kWh <sup>1)</sup>	<b>3.660</b> <sup>1)</sup>
<b>SCR Katalysator inkl. Zinsen (Zinssatz: 6 %)</b>			<b>11.300</b>
spezifische Katalysatorkosten [€/kg]		33 €/kg	
Menge des Katalysators [kg]	2.500		
durchschnittliche Lebensdauer des Katalysators [a]	10		
<b>flüssiger Ammoniak</b>			<b>262.650</b> <sup>2)</sup>
spezifische Kosten von fl. Ammoniak [€/t] <sup>2)</sup>		220 €/t <sup>2)</sup>	
Verbrauch an Ammoniak [kg/h]:	144		
<b>BEWERTETE JÄHRLICHE KOSTEN FÜR SCR [€/a]</b>			<b>340.900</b> <sup>2)</sup>
<b>SPEZIFISCHE MEHRKOSTEN BEZOGEN AUF DIE PRODUKTION [€/t HNO<sub>3</sub>]</b>			<b>1,89</b> <sup>2)</sup>
<b>SPEZIFISCHE MEHRKOSTEN BEZOGEN AUF DIE REDUKTION VON NO<sub>x</sub> [€/t NO<sub>x</sub>]</b>			<b>157</b> <sup>2)</sup>

<sup>1)</sup> Spezifische Kosten für elektrische Energie wurden vom Umweltbundesamt auf Basis früherer Studien (vgl. WIESENBERGER & KIRCHER, 2001) mit 0,044 €/kWh angenommen.

<sup>2)</sup> Spezifische Kosten von flüssigem NH<sub>3</sub> wurden vom Umweltbundesamt auf Basis früherer Studien (vgl. ECKER & WINTER, 2000) mit 220 €/t angenommen. In der Literatur sind spezifische Kosten von Ammoniak für die Emissionsminderung in HNO<sub>3</sub>-Anlagen im Bereich von 100 \$/t (SCHWEFER et al., 2000) und 200 €/t (POTTIER, 2001) angegeben. Die geringeren Kosten könnten möglicherweise darauf zurückgeführt werden, dass die Verfügbarkeit von NH<sub>3</sub> am Standort berücksichtigt wurde. Berücksichtigt man die geringeren Kosten in der oben angeführten Abschätzung so vermindern sich die jeweiligen Kosten um etwa 40 %.

## Primäre Maßnahmen zur NO<sub>x</sub> Emissionsminderung – Verbesserte Absorption

Ein hoher Umsatzgrad bei der Absorption lässt sich vor allem durch einen hohen Absorptionsdruck erzielen. Mit einem Absorptionsdruck von etwa 15 bar sind auch ohne Sekundär-minderungsverfahren Emissionen von **100–300 mg NO<sub>x</sub>/Nm<sup>3</sup>** (als NO<sub>2</sub>) erreichbar. Für Neuanlagen entspricht, falls kein SCR-Verfahren eingesetzt wird, ein Absorptionsdruck von etwa 15 bar dem Stand der Technik. In bestehenden Anlagen ist eine Erhöhung des Absorptionsdruckes prinzipiell nicht möglich.

Ein hoher Umsatzgrad bei der Absorption resultiert in einem entsprechend geringeren spezifischen Ammoniakverbrauch und einer geringeren NO<sub>x</sub>-Rohgaskonzentrationen im nachfolgenden SCR Reaktor. Absorptionsdrücke liegen üblicherweise bei Altanlagen bei mindestens 3–4 bar bzw. bei Neuanlagen bei über 8 bar<sup>1</sup>. Der Betrieb von Absorptionskolonnen unter Normaldruck entspricht nicht dem Stand der Technik.

Bis zu einem gewissen Ausmaß können NO<sub>x</sub> Emissionen auch durch Modifikationen der Bauweise der Absorptionskolonne<sup>2</sup> und durch niedrige Absorptionstemperaturen<sup>3</sup> reduziert werden. Mit diesen Maßnahmen sind jedoch wesentlich geringere Emissionsminderungen erreichbar, als mit dem SCR-Verfahren, weshalb diese Maßnahmen in erster Linie zusätzlich zur selektiven katalytischen Reduktion gesetzt werden.

## Nicht selektive katalytische Reduktion (NSCR)

Beim NSCR-Verfahren reagiert der in NO<sub>x</sub> oder N<sub>2</sub>O gebundene Sauerstoff an einem Katalysator mit Brennstoff (Erdgas oder Wasserstoff). Der Brennstoff reduziert NO<sub>2</sub> zu NO, womit eine Entfärbung des Abgases eintritt. Bevor eine weitere Reduktion von NO bzw. N<sub>2</sub>O erfolgt, muss jedoch der gesamte freie Sauerstoff im Abgas (1–4 vol. %) mit dem Brennstoff reagieren. In Folge dieser Reaktion von Brennstoff mit freiem Sauerstoff ergeben sich Verlagerungseffekte wie ein hoher Brennstoffbedarf sowie hohe Sekundäremissionen von CO, CO<sub>2</sub>, HCN und VOC. Aus diesem Grund entspricht das NSCR Verfahren für die NO<sub>x</sub>-Minderung bei Salpetersäureanlagen nicht dem Stand der Technik.

## N<sub>2</sub>O-Emissionen und Massnahmen zur Minderung von N<sub>2</sub>O Emissionen

Die Herstellung von Salpetersäure trägt wesentlich zu den Emissionen des Treibhausgases N<sub>2</sub>O bei. In Abhängigkeit der Verfahrensweise (Druck bei der katalytischen NH<sub>3</sub>-Oxidation) weisen die österreichischen Anlagen Emissionen von ca. 1.200 bzw. 2.750 mg N<sub>2</sub>O/Nm<sup>3</sup> auf.

Um die N<sub>2</sub>O-Bildung möglichst gering zu halten, ist ein hoher Umsatzgrad bei der katalytischen NH<sub>3</sub>-Oxidation von hoher Bedeutung. Der Umsatz der Ammoniak Oxidation hängt von Reaktionstemperatur, Arbeitsdruck, Gasgeschwindigkeit, Volumen des Katalysators sowie von der Reinheit der Gasströme von Luft und Ammoniak ab.

Für Neuanlagen ist ein patentiertes und kommerzialisiertes Verfahren zur Zersetzung von N<sub>2</sub>O im Reaktor für die katalytische NH<sub>3</sub>-Oxidation (homogene Zersetzung) verfügbar.

Im Rahmen verschiedener Forschungsvorhaben werden derzeit Verfahren zur Minderung von N<sub>2</sub>O-Emissionen entwickelt. Erste Erfolg versprechende Ergebnisse wurden vor allem für die katalytische Zersetzung von N<sub>2</sub>O im Reaktor für die katalytische NH<sub>3</sub>-Oxidation präsentiert. Das Verfahren, welches auch in bestehenden Anlagen eingesetzt werden könnte, wird bereits großtechnisch erprobt und könnte in naher Zukunft kommerziell verfügbar sein.

<sup>1</sup> Der Umsatzgrad liegt bei modernen Hochdruck-Absorptionskolonnen bei über 99,8 %.

<sup>2</sup> durch erhöhte Anzahl der Siebböden (Extended Absorption) oder durch höheren Flüssigkeitsstand in der Absorptionskolonne (High Efficiency Absorption)

<sup>3</sup> mit zusätzlichen Kühleinrichtungen

In Tabelle III sind verfügbare und in Entwicklung befindliche Verfahren zur Reduktion von N<sub>2</sub>O-Emissionen aus Salpetersäureanlagen zusammengestellt. In der Tabelle ist der Entwicklungsstand (3/2001) dieser Technologien angegeben.

Tabelle III: Zusammenstellung von verfügbaren und in Entwicklung befindlichen Verfahren zur Reduktion von N<sub>2</sub>O Emissionen aus Salpetersäureanlagen mit Entwicklungsstand (3/2001)

charakteristische Merkmale	Entwicklungsstand (3/2001)	(erwartete) N <sub>2</sub> O Reduktion	Literatur
<b>Maßnahmen zur Reduktion der N<sub>2</sub>O Bildung – primäre Maßnahmen</b>			
<ul style="list-style-type: none"> <li>Modifikation der Netzgeometrie der Pt/Rh-Katalysatoren</li> <li>Co<sub>3</sub>O<sub>4</sub> Katalysator für die Oxidation von Ammoniak</li> </ul>	<p>Katalysatoren mit modifizierter Netzgeometrie werden von Herstellern angeboten</p> <p>?</p>	?	<p>Schwefer et al. (2000)</p> <p>Schwefer et al. (2000)</p>
<b>Verfahren zur Zersetzung von N<sub>2</sub>O im Reaktor zur katalytischen Ammoniakverbrennung – sekundäre Maßnahmen</b>			
<ul style="list-style-type: none"> <li>homogene Zersetzung von N<sub>2</sub>O im Reaktor für die katalytische NH<sub>3</sub>-Oxidation</li> <li>katalytische Zersetzung von N<sub>2</sub>O im Reaktor für die katalytische NH<sub>3</sub>-Oxidation</li> </ul>	<p>patentiertes Verfahren; kommerziell verfügbar</p> <p>70–85 %</p>	70–85 %	<p>Schöffel et al. (2001); Kongshaug (1998).</p> <p>Kuhn (2001)</p> <p>Schöffel et al. (2001)</p>
<b>Verfahren zur Zersetzung/Reduktion von N<sub>2</sub>O im Abgas (nach dem Absorptionsturm) – tertiäre Maßnahmen</b>			
<ul style="list-style-type: none"> <li>Nicht-selektive katalytische Reduktion (NSCR)</li> <li>katalytische Zersetzung</li> <li>katalytische Reduktion</li> </ul>	<p>in einigen älteren Anlagen eingesetztes Verfahren zu NO<sub>x</sub> Minderung; entspricht nicht dem Stand der Technik</p> <p>Versuche im Labormaßstab (Modellgas) und Versuchsbetrieb von Pilotanlagen (Teilabgasstrom einer Salpetersäureanlage)</p>	~ 85 %	<p>Schwefer et al. (2000) Dittmar (1985).</p> <p>Schwefer et al. (2000) Maurer &amp; Groves (2001); Mul et al. (2001), Kieger et al. (2001); van den Brink (2001); van d. Brink et al (2000).</p>

## Abwasser

Bei der Herstellung von Schwachsäure wird das Prozesswasser vollständig im Absorber für die Herstellung von Salpetersäure wiedereingesetzt. Emissionen von periodischen Ausblase- und Reinigungsprozessen werden gesammelt und in die Produktion rückgeführt. Bei der Herstellung von konzentrierter Salpetersäure entsteht Prozesswasser, welches nicht vollständig im Produktionsprozess wiedereingesetzt werden kann.

## Abfälle und Reststoffe

Folgende Abfälle und Reststoffe sowie deren entsprechende Behandlung/Entsorgung sind bei der Herstellung von Salpetersäure von Bedeutung:

- Gebrauchte Filtermaterialien werden gereinigt und wiedereingesetzt oder entsorgt. Der Wiedereinsatz von gebrauchten Filtermaterialien sollte jedoch nicht die Abscheideleistung der Filter beeinträchtigen.
- Altöle fallen bei der regelmäßigen Erneuerung von hydraulischen Ölen für Pumpen und Kompressoren bzw. aus der Kontamination von Ammoniak mit Hydraulikölen an. Altöle erfordern eine entsprechende Entsorgung.
- Verbrauchte Katalysatoren sowie Rückgewinnungssysteme für Edelmetalle werden extern verwertet.

## Salpetersäureherstellung in Österreich

In Österreich wird Salpetersäure (Schwachsäure – 59.7 % HNO<sub>3</sub>) an einem Standort in zwei Anlagen (N/M Verfahren und M/H Verfahren) hergestellt. Die Gesamtkapazität beträgt 480.000 t/a (100 %ige HNO<sub>3</sub>). Etwa 95 % der HNO<sub>3</sub> Produktion wird für die Herstellung von Düngemitteln auf Basis NPK (Mehrnährstoffdünger) und KAS (Kalkammoniumsalpeter) eingesetzt. Die Herstellung von technischem Ammoniumnitrat ist ebenfalls von Bedeutung.

Tabelle III: Überblick über österreichische Anlagen zur Herstellung von Salpetersäure  
[AGROLINZ, 1999, AGROLINZ 2000]

	Linie E (M/H Verfahren)	Linie F (N/M Verfahren)
Kapazität <sup>2)</sup>	300.000 t/a	180.000 t/a
NH <sub>3</sub> -Input (1998)	91.700 t	52.330 t
Produktion (1998) von HNO <sub>3</sub> <sup>2)</sup>	321.400 t	183.430 t
Druck bei der katalytischen Oxidation von NH <sub>3</sub>	3,3 barü	- 0,08 barü
Oxidationstemperatur	895 °C	840–850 °C
Absorptionsdruck	8 barü	3,8 barü
Absorptionstemperatur	25 °C	25 °C
Abgasvolumenstrom	112.000 Nm <sup>3</sup> /h	65.500 Nm <sup>3</sup> /h
Verfahren zur Minderung von NO <sub>x</sub> Emissionen	SCR	SCR
NO <sub>x</sub> Reingaskonzentration [mg/Nm <sup>3</sup> ] <sup>1)</sup> [kg NO <sub>x</sub> /t HNO <sub>3</sub> ] <sup>1) 2)</sup>	180–190 mg/Nm <sup>3</sup> 0,54–0,56 kg/t HNO <sub>3</sub>	320–330 mg/Nm <sup>3</sup> 0,98–0,99 kg/t HNO <sub>3</sub>
NH <sub>3</sub> Emissionen [mg NH <sub>3</sub> /Nm <sup>3</sup> ]	0,26–2,6 mg/Nm <sup>3</sup>	0,05–0,10 mg/Nm <sup>3</sup>
N <sub>2</sub> O Konzentration im Abgas [mg/Nm <sup>3</sup> ] [kg/t HNO <sub>3</sub> ] <sup>2)</sup>	1.960–2.750 mg/Nm <sup>3</sup> 5,8–8,1 kg/t HNO <sub>3</sub>	1.180–1.570 mg/Nm <sup>3</sup> 3,6–4,8 kg/t HNO <sub>3</sub>

<sup>1)</sup> als NO<sub>2</sub>      <sup>2)</sup> bezogen auf 100 %ige Salpetersäure

## SUMMARY AND CONCLUSIONS

### Object of the Study

The aim of this study is to describe state-of-the-art technologies for nitric acid production in view of the IPPC-directive. The study gives a general survey of applied technologies, starting materials, and emissions (incl. wastes and residual materials) specific to the production of nitric acid. An essential feature of the study is to point out the potential of reduction of atmospheric pollutants. Process integrated measures and end-of-pipe technologies for the reduction of air emissions are described. Cost estimates for selected end-of-pipe technologies are given. The specific situation in Austria is described.

### Production of Nitric Acid

Processes for the production of nitric acid are based on the Ostwald process. The ammonia, initially, is converted to nitric oxide over the precious metal gauze, and the nitric oxide is, subsequently, oxidised and absorbed in water to form nitric acid.

**Weak nitric acid** is produced with concentrations of up to 69.2 %. A major part of the nitric acid produced is used for the production of mineral fertilisers (NPK-fertilisers, calcium ammonium nitrate). Weak nitric acid also is used for the production of ammonium nitrate and adipic acid (starting material for nylon and polyester). Process technologies for weak nitric acid production differ mainly with regard to working pressure levels. Pressures are classified in:

- N: normal (atmospheric) pressure; only applied for catalytic ammonia oxidation
- M: medium pressure (3–6 bar) and
- H: high pressure (> 8 bar).

Figure I is a simplified schematic representation of weak acid production. Generally, two types of plants can be distinguished: single pressure and dual pressure plants.

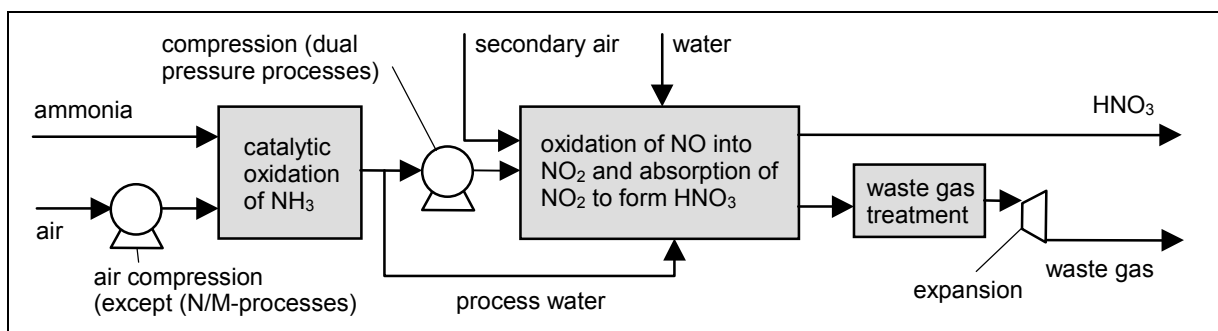


Figure I: Simplified schematic representation of weak nitric acid production

At **single pressure plants**, catalytic oxidation of ammonia takes place at the same pressure as absorption. M/M processes (medium pressure for NH<sub>3</sub> oxidation and for absorption) and H/H processes (high pressure for NH<sub>3</sub> oxidation and for absorption) are in operation.

At **dual pressure plants**, catalytic oxidation of ammonia takes place at a lower pressure than absorption. Usually M/H processes (medium pressure for NH<sub>3</sub> oxidation and high pressure for absorption) are in operation. Some N/M processes (normal pressure for NH<sub>3</sub> oxidation and medium pressure for absorption) are in operation.

The process technology of weak nitric acid production is relevant for emission and consumption levels. Dual pressure processes are more efficient than single pressure plants. A low (and medium) pressure level for the ammonia oxidation favours the conversion of  $\text{NH}_3$  to  $\text{NO}$ , resulting in higher efficiencies and lower  $\text{N}_2\text{O}$  emissions. High pressure at the absorption section favours the absorption and results in higher efficiency and lower  $\text{NO}_x$  concentrations in the waste gas.

**Concentrated nitric acid** is produced by indirect processes (concentrating weak nitric acid) or by direct processes (production of liquid  $\text{N}_2\text{O}_4$  which reacts under pressure with oxygen and dilutes nitric acid to form  $\text{HNO}_3$ ). Production of concentrated nitric acid by distillation of weak nitric acid is not possible.

## Starting Materials

Starting materials for the production of nitric acid are ammonia (280–290 kg  $\text{NH}_3$ /t  $\text{HNO}_3$ , depending on process technology), water and air. A considerable loss of precious metal takes place particularly in plants with ammonia oxidation at medium or high pressures. Lost precious metals are recovered by recovery systems installed at the catalytic reactor.

## Energy

Nitric acid production according to state-of-the-art technology is characterised by a **high degree of energy recovery**. A modern dual pressure nitric plant has a net energy output of 11 GJ/t  $\text{HNO}_3$ -N as high-pressure steam, corresponding to about 2.4 GJ/t  $\text{HNO}_3$  (100 %).

## $\text{NO}_x$ Emissions and Emission Reduction

$\text{NO}_x$  concentration after the absorption section mainly depends on the pressure applied at the absorption section. Low  $\text{NO}_x$  emission levels can be achieved by high absorption efficiencies (e.g. by the application of high absorption pressures) and/or by end-of-pipe technologies. For reduction of  $\text{NO}_x$ -emissions most nitric acid plants are equipped with end-of-pipe technologies. Among end-of-pipe measures, the **selective catalytic reduction (SCR) process is state-of-the-art technology for the reduction of  $\text{NO}_x$  emissions**. The non-selective catalytic reduction (NSCR) process cannot be considered state-of-the-art technology, as cross media effects occur, such as high secondary emissions and high fuel consumption levels. Alkaline final absorption processes are not state-of-the-art technology. Selective non-catalytic reduction (SNCR) processes are not applied for  $\text{NO}_x$  reduction in nitric acid plants.

### Selective Catalytic Reduction (SCR)

Nitrogen oxides of the waste gas selectively react to a catalyst with ammonia provided as a reducing agent. Emission reduction rates of up to 95 % can be achieved with the SCR process. SCR can be considered state-of-the-art technology for new and existing plants. For new plants a combination of SCR process and high-pressure absorption (< 8 bar) can be considered state-of-the-art technology.

At plants with **high-pressure absorption** (< 8 bar), **SCR** processes allow  $\text{NO}_x$  emissions of **100–200 mg  $\text{NO}_x/\text{Nm}^3$**  (as  $\text{NO}_2$ ). Table I presents estimates of main costs for retrofitting an SCR reactor at an existing M/H plant.

Table I: Main costs for retrofitting an SCR reactor at an existing nitric acid plant (M/H dual pressure plant); a production of 900 t HNO<sub>3</sub>/d, a waste gas volume of 110,000 Nm<sup>3</sup>/h, an NO<sub>x</sub> reduction of 0.3 g NO<sub>x</sub>/Nm<sup>3</sup> (indicated as NO<sub>2</sub>) and a clean gas concentration of less than 200 mg NO<sub>x</sub>/Nm<sup>3</sup> (indicated as NO<sub>2</sub>) are assumed.

		€/unit	€/a
<b>operating parameter:</b>			
waste gas volume [Nm <sup>3</sup> /h]	110,000		
operating time [h/a]	8,400		
NO <sub>x</sub> concentration in crude gas [mg/Nm <sup>3</sup> as NO <sub>2</sub> ]	500		
NO <sub>x</sub> concentration in clean gas [mg/Nm <sup>3</sup> as NO <sub>2</sub> ]	200		
<b>investment costs excl. catalyst [€]</b>	<b>925,000</b>		
<b>repayment on investment incl. interest</b>			<b>95,400</b>
period of depreciation [a]	15		
interest rate [%]	6		
<b>maintenance and wear:</b>			<b>18,500</b>
maintenance and wear [% of investment costs]	2		
<b>energy consumption:</b>			
working pressure [bar]	9		
pressure drop of SCR reactor [mbar]	10		
working temperature of SCR reactor [°C]	190		
<b>extra energy consumption of compressor due to SCR reactor [kWh/h]<sup>1)</sup></b>	<b>8</b>	<b>0.044 €/kWh<sup>1)</sup></b>	<b>3,050<sup>1)</sup></b>
<b>additional energy consumers [kWh/h]<sup>1)</sup></b>	<b>10</b>	<b>0.044 €/kWh<sup>1)</sup></b>	<b>3,660<sup>1)</sup></b>
<b>SCR catalyst incl. interest (interest rate: 6 %)</b>			<b>8,300</b>
specific catalyst costs [€/kg]		18 €/kg	
amount of catalyst [kg]	3,400		
lifetime of catalyst [a]	10		
<b>liquid ammonia<sup>2)</sup></b>			<b>35,500<sup>2)</sup></b>
ammonia consumption [kg/h]:	20		
specific costs of liquid ammonia <sup>2)</sup>		220 €/t <sup>2)</sup>	
<b>ESTIMATED ANNUAL COSTS FOR SCR [€/a]</b>			<b>164,400<sup>2)</sup></b>
<b>SPECIFIC EXTRA COSTS REFERRING TO PRODUCED HNO<sub>3</sub> [€/t HNO<sub>3</sub>]</b>			<b>0.55<sup>2)</sup></b>
<b>SPECIFIC EXTRA COSTS FOR NO<sub>x</sub> ABATEMENT [€/t NO<sub>x</sub>]</b>			<b>593<sup>2)</sup></b>

<sup>1)</sup> Specific costs for electric energy of 0.044 €/kWh were calculated by the Federal Environment Agency Austria on basis of previous studies (cf. WIESENBERGER & KIRCHER, 2001).

<sup>2)</sup> Specific costs for liquid ammonia of 220 €/t were calculated by the Federal Environment Agency Austria on basis of previous studies (cf. ECKER & WINTER, 2000). In literature specific costs of ammonia for the emission control in nitric acid plants are indicated in the range between 100 \$/t (SCHWEFER et al., 2000) and 200 €/t (POTTIER, 2001). The lower costs might be due to the fact, that ammonia is available on-site at a nitric acid plant. Calculating lower ammonia costs in the table above will decrease annual costs and specific extra costs for the SCR installation by about 15 %.



By application of **SCR** processes at plants **with medium pressure absorption** (4–8 bar) emissions of **200–350 mg NO<sub>x</sub>/Nm<sup>3</sup>** (as NO<sub>2</sub>) are achievable. Table II presents estimates of main costs for an SCR installation in the course of adaptation of an old normal pressure plant (by construction of a new medium pressure absorption column).

*Table II: Main costs of an SCR installation in course of the adaptation of an old normal pressure plant (by construction of a new medium pressure absorption column); a production of 500 t/d, a waste gas volume of 65,000 Nm<sup>3</sup>/h, a crude gas concentration of 4,000–6,000 mg NO<sub>x</sub>/Nm<sup>3</sup> (as NO<sub>2</sub>) and a clean gas concentration of less than 350 mg NO<sub>x</sub>/Nm<sup>3</sup> (as NO<sub>2</sub>) are assumed.*

		€/unit	€/a
<b>operating parameter:</b>			
waste gas volume [Nm <sup>3</sup> /h]	65,000		
operating time [h/a]	8,400		
NO <sub>x</sub> concentration in crude gas [mg/Nm <sup>3</sup> as NO <sub>2</sub> ]	4,300		
NO <sub>x</sub> concentration in clean gas [mg/Nm <sup>3</sup> as NO <sub>2</sub> ]	320		
<b>investment costs excl. catalyst [€]</b>	<b>353,200</b>		
<b>repayment on investment incl. interest</b>			<b>36,400</b>
period of depreciation	15		
interest rate [%]	6		
<b>maintenance and wear:</b>			<b>7,060</b>
maintenance and wear [% of investment costs]	2		
<b>energy consumption:</b>			
working pressure (bar)	4.8		
pressure drop of SCR reactor (mbar)	50		
working temperature of SCR reactor (°C)	270		
<b>extra energy consumption of compressor, due to SCR reactor [kWh/h]<sup>1)</sup></b>	54	0.044 €/kWh <sup>1)</sup>	<b>19,830<sup>1)</sup></b>
<b>additional energy consumers [kWh/h]<sup>1)</sup></b>	10	0.044 €/kWh <sup>1)</sup>	<b>3,660<sup>1)</sup></b>
<b>SCR catalyst incl. interest (interest rate: 6 %)</b>			<b>11,300</b>
specific catalyst costs [€/kg]		33 €/kg	
amount of catalyst [kg]	2,500		
lifetime of catalyst [a]	10		
<b>liquid ammonia</b>			<b>262,650<sup>2)</sup></b>
specific costs of liquid ammonia [€/t] <sup>2)</sup>		220 €/t <sup>2)</sup>	
ammonia consumption [kg/h]:	144		
<b>ESTIMATED ANNUAL COSTS FOR SCR [€/a]</b>			<b>340,900<sup>2)</sup></b>
<b>SPECIFIC EXTRA COSTS REFERRING TO PRODUCED HNO<sub>3</sub> [€/t HNO<sub>3</sub>]</b>			<b>1.89<sup>2)</sup></b>
<b>SPECIFIC EXTRA COSTS FOR NO<sub>x</sub> ABATEMENT [€/t NO<sub>x</sub>]</b>			<b>157<sup>2)</sup></b>

<sup>1)</sup> Specific costs for electric energy of 0.044 €/kWh were calculated by the Federal Environment Agency Austria on basis of previous studies (cf. WIESENBERGER & KIRCHER, 2001).

<sup>2)</sup> Specific costs for liquid ammonia of 220 €/t were calculated by the Federal Environment Agency Austria on basis of previous studies (cf. ECKER & WINTER, 2000). In literature specific costs of ammonia for the emission control in nitric acid plants are indicated in the range between 100 \$/t (SCHWEFER et al., 2000) and 200 €/t (POTTIER, 2001). The lower costs might be due to the fact, that ammonia is available on-site at a nitric acid plant. Calculating lower ammonia costs in the table above will decrease annual costs and specific extra costs for the SCR installation by about 40 %.

## Process Integrated Measures for NO<sub>x</sub> Emission Reduction – Measures for Achieving High Absorption Efficiencies

High absorption efficiencies mainly result from high absorption pressure. By application of pressures of about 15 bar emissions of **100–300 mg NO<sub>x</sub>/Nm<sup>3</sup>** (as NO<sub>2</sub>) are achievable without end-of-pipe techniques. The application of absorption pressures of about 15 bar can be considered state-of-the-art technology for new plants, in case an SCR process is not installed. Existing nitric acid plants do not allow an increase of the absorption pressure.

High absorption efficiencies are important to minimise ammonia consumption levels as well as to minimise NO<sub>x</sub> inlet concentration of a following SCR device. Usually absorption pressures are at least 3–4 bar (old plants) or above 8 bar (new plants)<sup>4</sup>. Absorption columns operating at normal (atmospheric) pressure are not in accordance with state-of-the-art technology.

To a certain degree, NO<sub>x</sub> emissions can be reduced by the modification of the design of the absorption column<sup>5</sup> and by low absorption temperatures<sup>6</sup>. NO<sub>x</sub> reduction rates of these measures are considerable lower than reduction rates of SCR technology. These measures are in particular applied in combination with selective catalytic reduction.

### Non-selective Catalytic Reduction (NSCR)

NSCR is based on the catalytic reaction of fuel (natural gas or hydrogen) with oxygen bound in NO<sub>x</sub> and N<sub>2</sub>O. On a catalyst, fuel reduces NO<sub>2</sub> into NO, resulting in a discoloration of the waste gas. However, the fuel has to react completely with free oxygen present in the waste gas (1–4 vol. %) before a reduction of NO and N<sub>2</sub>O takes place. Due to this reaction of fuel with free oxygen cross media effects occur, such as high fuel consumption levels and high secondary emissions of CO, HCN, CO<sub>2</sub> and VOC. For that reason, the NSCR process cannot be considered state-of-the-art technology for the reduction of NO<sub>x</sub> emissions at nitric acid plants.

### N<sub>2</sub>O Emissions and Emission Reduction

Nitric acid production is a major polluter contributing to the emission of the greenhouse gas N<sub>2</sub>O. Austrian nitric acid plants have emission levels between 1,200–2,750 mg N<sub>2</sub>O/Nm<sup>3</sup>, depending on process technology (pressure level of the catalytic ammonia oxidation).

Generally, a high efficiency of the catalytic ammonia oxidation is important to reduce N<sub>2</sub>O formation. The efficiency of the ammonia conversion is a function of temperature, pressure, velocity of gas stream, volume of catalyst, and purity of the ammonia and air streams.

A commercialised and patented process for the decomposition of N<sub>2</sub>O in the NH<sub>3</sub> combustion unit (homogenous decomposition) is available for new nitric acid plants.

Several projects are run by industry and research institutes for developing N<sub>2</sub>O abatement processes. First promising results have been reported in particular on catalytic decomposition processes of N<sub>2</sub>O in the ammonia combustion unit. This process would also be suitable for retrofitting into existing nitric acid plants. Catalysts for the catalytic N<sub>2</sub>O decomposition in the ammonia conversion unit are already being tested on a technical scale and might be available in the near future.

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<sup>4</sup> Absorption yield in new plants with high pressure absorption columns is above 99,8 %.

<sup>5</sup> by increasing the number of sieve trays (Extended Absorption) or by increasing the height of the liquid emulsion (High Efficiency Absorption)

<sup>6</sup> with additional cooling equipment

Table III presents a summary on available and emerging techniques for the abatement of N<sub>2</sub>O emissions from nitric acid plants. In the table the status (3/2001) of these techniques is indicated.

Table III: Summary of available and emerging techniques for the N<sub>2</sub>O abatement from nitric acid plants including the status (3/2001) of these techniques

Characteristics	Current status (3/2001)	(Expected) N <sub>2</sub> O reduction	References
<b>Measures for the reduction of N<sub>2</sub>O formation – primary measures</b>			
<ul style="list-style-type: none"> <li>Modifications of the gauze geometry and density of Pt/Rh catalysts</li> </ul>	catalysts with knitted gauzes are provided by catalyst manufacturer	?	Schwefer et al. (2000)
<ul style="list-style-type: none"> <li>CO<sub>3</sub>O<sub>4</sub> catalyst for the NH<sub>3</sub> combustion</li> </ul>	?	~ 80 %	Schwefer et al. (2000)
<b>Processes for the decomposition of N<sub>2</sub>O in the NH<sub>3</sub>-combustion unit – secondary measures</b>			
<ul style="list-style-type: none"> <li>Homogenous decomposition</li> </ul>	patented process; commercially available	70–85 %	Schöffel et al. (2001); Kongshaug (1998).
<ul style="list-style-type: none"> <li>Catalytic decomposition of N<sub>2</sub>O in the NH<sub>3</sub>-combustion unit</li> </ul>	full scale trial at three plants since 3/1999, 7/1999 and 1/2000;	~ 80 %	Kuhn (2001)
	full scale trial at one plant since 5/2000	~ 90 %	Schöffel et al. (2001)
<b>Processes for the decomp./reduction of N<sub>2</sub>O in the tail gas (downstream the absorption unit) – tertiary measures</b>			
<ul style="list-style-type: none"> <li>Non-selective catalytic reduction (NSCR)</li> </ul>	NO <sub>x</sub> abatement process installed at some older plants; NSCR cannot be considered state-of-the-art technology	~ 85 %	Schwefer et al. (2000) Dittmar (1985).
<ul style="list-style-type: none"> <li>Catalytic decomposition</li> </ul>	tests on laboratory scale (model tail gas) and tests at pilot plants (side stream of the waste gas of a nitric acid plant)	depending on temperature and catalyst	Schwefer et al. (2000) Maurer & Groves (2001); Mul et al. (2001), Kieger et al. (2001); van den Brink et al. (2000); van den Brink (2001)
<ul style="list-style-type: none"> <li>Catalytic reduction</li> </ul>	requires reducing agent such as NH <sub>3</sub> , propane (LPG) or natural gas		

## Wastewaters

At the production of weak nitric acid, all process condensates are transferred to the absorption column and reused for nitric acid production. Emissions from the purging points and from periodic blow-down processes are collected and reprocessed. At the production of concentrated nitric acid process condensates arise, which cannot be completely reused in the process.

## Wastes and Residues

Wastes and residues arising from the production of nitric acid are listed below and should be dealt with as follows:

- Used filter materials can be cleaned and reused or are disposed. However, reusing filter material should not reduce the efficiency of the filtering installations.
- Waste oils arising from periodical replacement of lubricating oil of rotating machines and from contamination of ammonia with hydraulic oils (compressors of ammonia plant). Waste oils demand adequate disposal.
- Spent oxidation catalysts and catalyst recovery gauzes are reprocessed.

## Nitric Acid Production in Austria

In Austria, weak nitric acid (59.7 % HNO<sub>3</sub>) is produced in two plants (N/M process and M/H process) in one location. The entire capacity of HNO<sub>3</sub> production is about 480.000 t/a (based on 100 % HNO<sub>3</sub>). About 95 % of the nitric acid is used as raw material to produce NPK and ammonium nitrate based fertilisers. The production of technical ammonium nitrate is also of relevance.

Table III: Summary of the Austrian nitric acid plants [AGROLINZ, 1999, AGROLINZ 2000]

		Line E (M/H process)	line F (N/M process)
Capacity <sup>3)</sup>		300,000 t/a	180,000 t/a
NH <sub>3</sub> input 1998		91,700 t	52,330 t
HNO <sub>3</sub> production <sup>3)</sup> (1998)		321,400 t	183,430 t
Pressure for catalytic NH <sub>3</sub> oxidation <sup>1)</sup>		3.3 bar	- 0.08 bar
Oxidation temperature		895 °C	840–850 °C
Pressure for absorption <sup>1)</sup>		8 bar	3.8 bar
Absorption temperature		25 °C	25 °C
Waste gas volume		112,000 Nm <sup>3</sup> /h	65,500 Nm <sup>3</sup> /h
NO <sub>x</sub> reduction process		SCR	SCR
NO <sub>x</sub> concentration after SCR reactor	[mg/Nm <sup>3</sup> ] <sup>2)</sup> [kg NO <sub>x</sub> /t HNO <sub>3</sub> ] <sup>2) 3)</sup>	180–190 mg/Nm <sup>3</sup> 0.54–0.56 kg/t HNO <sub>3</sub>	320–330 mg/Nm <sup>3</sup> 0.98–0.99 kg/t HNO <sub>3</sub>
NH <sub>3</sub> slip	[mg NH <sub>3</sub> /Nm <sup>3</sup> ]	0.26–2.6 mg/Nm <sup>3</sup>	0.05–0.10 mg/Nm <sup>3</sup>
N <sub>2</sub> O–concentration in waste gas	[mg/Nm <sup>3</sup> ] [kg/t HNO <sub>3</sub> ] <sup>3)</sup>	1,960–2,750 mg/Nm <sup>3</sup> 5.8–8.1 kg/t HNO <sub>3</sub>	1,180–1,570 mg/Nm <sup>3</sup> 3.6–4.8 kg/t HNO <sub>3</sub>

<sup>1)</sup> pressure above atmospheric

<sup>2)</sup> as NO<sub>2</sub>

<sup>3)</sup> related to 100 % HNO<sub>3</sub>

# 1 INTRODUCTION

## 1.1 Object of the Study

The aim of this study is to describe state-of-the-art technologies for nitric acid production in view of the IPPC-directive. The study gives a general survey of applied technologies, starting materials, and emissions (incl. wastes and residual materials) specific to the production of nitric acid. An essential feature of the study is to point out the potential of reduction of atmospheric pollutants. Process integrated measures and end-of-pipe technologies for the reduction of air emissions are described. Cost estimates for selected end-of-pipe technologies are given. The specific situation in Austria is described.

## 1.2 Reference to the IPPC-Directive

According to Art. 2 Number 11 of the European Council Directive on Integrated Pollution Prevention and Control IPPC (Directive 96/61/EC of 24 September 1996) "best available technique" ("BAT") shall mean the most effective and advanced stage in the development of activities and their methods of operation, which indicate the practical suitability of particular techniques for providing in principle the basis for emission limit values designed to prevent and, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole.

The term "techniques" shall include both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned.

"Available" techniques shall mean those developed on a scale which allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced inside the Member State in question, as long as they are reasonably accessible to the operator.

"Best" shall mean most effective techniques in achieving a high general level of protection of the environment as a whole.

According to the European Council Directive 96/61/EC concerning integrated pollution prevention and control Annex IV, the following considerations should be taken into account when determining best available techniques:

- the use of low-waste technologies;
- the use of less hazardous technologies;
- the furthering of recovery and recycling of substances generated and used in the process and of waste, when appropriate;
- comparable processes, facilities or methods of operations which have been tried with success on an industrial scale;
- technological advances and changes in scientific knowledge and understanding;
- the nature, effects and volume of emissions concerned;
- the commissioning dates for new or existing installations;
- the length of time needed to introduce the best available technique;
- the consumption and nature of raw materials (including water) used in the process and their energy efficiency;

- the need to prevent or reduce to a minimum the overall impact of emissions on the environment and the risks to it;
- the need to prevent accidents and to minimise the consequences for the environment;
- the information published by the Commission pursuant to Article 16 (2) or by international organisations.

According to Art. 16 Number 2 of the Council Directive 96/61/EC of 24 September 1996 concerning integrated pollution prevention and control (IPPC), the European Commission organises an exchange of information between Member States and the industry concerning best available techniques, associated monitoring, and developments.

The information structure for BAT is based on the Information Exchange Forum (IEF), on Technical Working Groups (TWGs) and on the European Integrated Pollution Prevention and Control Bureau (EIPPCB). The IEF co-ordinates the information exchange on BAT. It evaluates the results of the exchange of information as presented in the form of draft IPPC BAT reference documents (BREF). The Technical Working Groups are groups of experts established by the Commission after consultation with the IEF to work out details regarding the exchange of information on industrial activities. The EIPPCB provides the TWG with technical and administrative support. The EIPPCB is located at the Institute for Prospective Technology Studies IPTS in Seville.

In all probability, the kick-off meeting of the Technical Working Group for Large Volume Inorganic Gaseous and Liquid Chemistry will take place in the year 2000. This Technical Working Group will deal with the production of nitric acid.

### 1.3 Historical Aspects

Until the end of the 19<sup>th</sup> century, nitric acid was produced by reaction of sulphuric acid with saltpetre according to the process of Glauber.

As stocks of saltpetre were considered exhausted at the beginning of the 20<sup>th</sup> century, processes for industrial production were developed. In this context, the process of air oxidation by electric arc according to Birkeland-Eyde deserves to be mentioned. Owing to its low energy efficiency, this process was replaced by the catalytic ammonia oxidation.

C.F. Kuhlmann (1838) discovered the principle of catalytic ammonia oxidation by platinum catalysis. Industrial production of nitric acid by catalytic ammonia oxidation became important with the invention of ammonia synthesis according to Haber-Bosch. Around 1900, Ostwald developed the catalytic oxidation of ammonia on a commercial scale. Currently, all producers use this process.

### 1.4 Production and Use of Nitric Acid

Nitric acid is commercially available in two forms: weak nitric acid (< 69.2% HNO<sub>3</sub>) and concentrated nitric acid (> 95 % HNO<sub>3</sub>). Different processes are required to produce these two forms of acid.

Production of nitric acid in the European Community is about 20 Mt/a. About 30 plants are in operation [CEFIC 2000]. Weak nitric acid is produced in far greater quantities than concentrated nitric acid.

Nitric acid is an intermediate for the production of inorganic and organic chemicals. Figure 1 shows an overall view of the use of weak nitric acid and concentrated nitric acid.

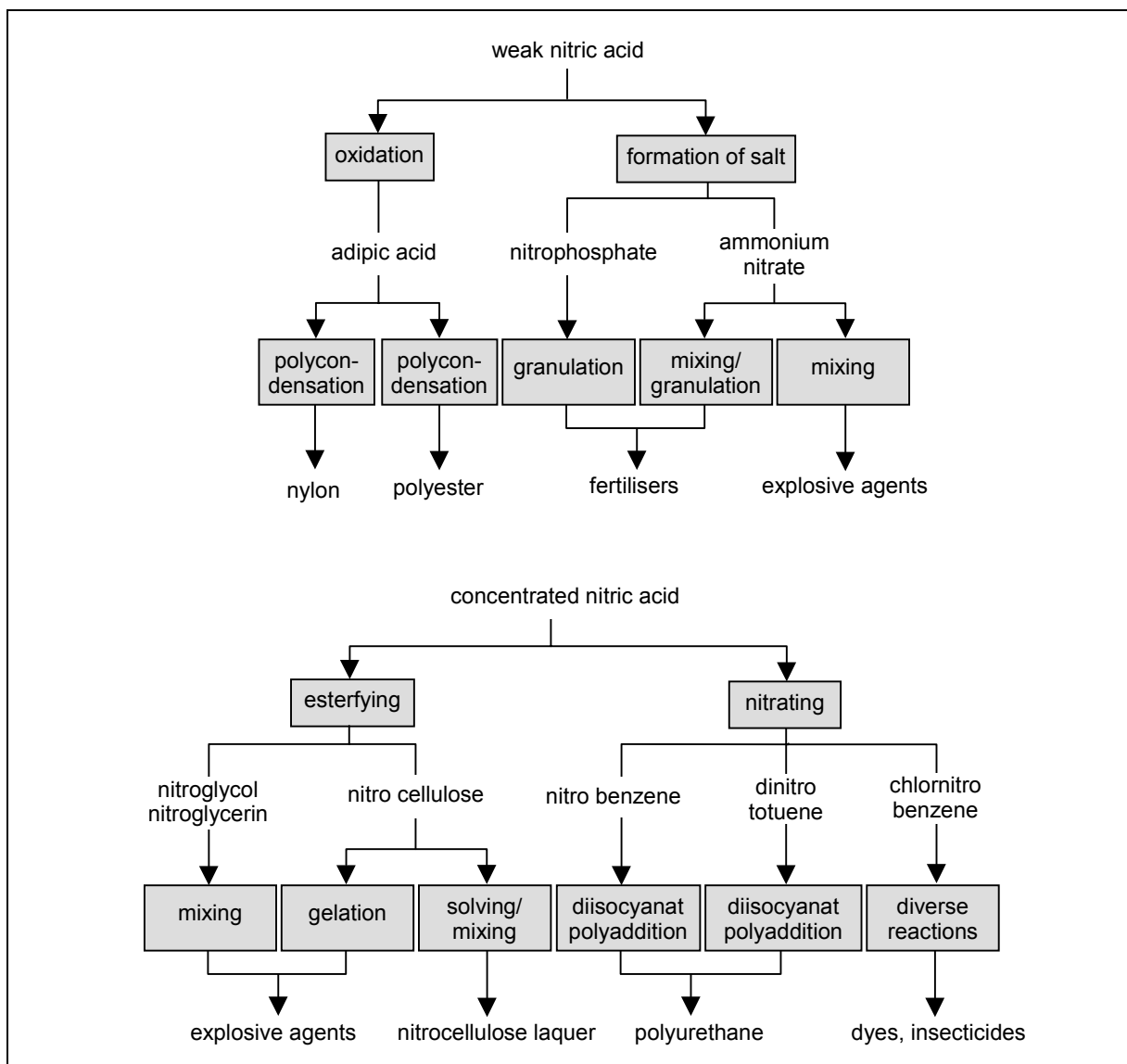


Figure 1: Overall view of the use of weak nitric acid and concentrated nitric acid according to [FLEISCHER 1995]

## 1.5 Production and Consumption of Nitric Acid in Austria

In Austria, weak nitric acid is produced with a concentration of 59,6%  $\text{HNO}_3$  by oxidation of ammonia. Two nitric acid plants are in operation at one site. These nitric acid plants process ammonia which is produced in the same location. The annual production based on 100 %  $\text{HNO}_3$  was 489,000 t in 1997 and 505,000 t in 1998. There is no production of concentrated nitric acid in Austria. Plants for producing concentrated acid were closed down several years ago. Nitric acid is mainly used for the production of fertilisers. About 95 % of the nitric acid is used as raw material to produce NPK and calcium ammonium nitrate based fertilisers. The production of technical ammonium nitrate is of relevance, as well.

## 2 TECHNOLOGY OF NITRIC ACID PRODUCTION

The following describes processes for nitric acid production by catalytic oxidation of ammonia. For a detailed description of nitric acid production, the reader is referred to [THIEMANN et. al 1991].

Processes for the production of nitric acid are based on the Ostwald process, in which ammonia is oxidised with air to form nitric monoxide (NO). Nitric oxide (NO) is further oxidised to form nitrogen dioxide (NO<sub>2</sub>) which finally is absorbed in water to produce HNO<sub>3</sub>.

The main part of the nitric acid is produced as **weak nitric acid**, which has concentrations of up to 69.2 % and is used for the production of fertilisers. Due to different thermodynamic conditions for ammonia combustion and absorption, process technologies differ with regard to working pressure levels. Pressures are classified in:

- N: normal pressure; only applied for ammonia oxidation
- M: medium pressure (3–6 bar) and
- H: high pressure (> 8 bar).

Generally, two types of plants can be distinguished: single pressure plants and dual pressure plants:

With **single pressure plants**, oxidation of ammonia takes place at the same pressure as oxidation and absorption. M/M processes (medium pressure for NH<sub>3</sub> oxidation and for absorption) and H/H processes (high pressure for NH<sub>3</sub> oxidation and for absorption) are in operation.

With **dual pressure plants**, oxidation of ammonia takes place at a lower pressure than absorption. M/H processes (medium pressure for NH<sub>3</sub> oxidation and high pressure for absorption) are in operation. Some N/M processes (normal pressure for NH<sub>3</sub> oxidation and medium pressure for absorption) are in operation.

A simplified schematic representation of weak acid production is given in figure 2.

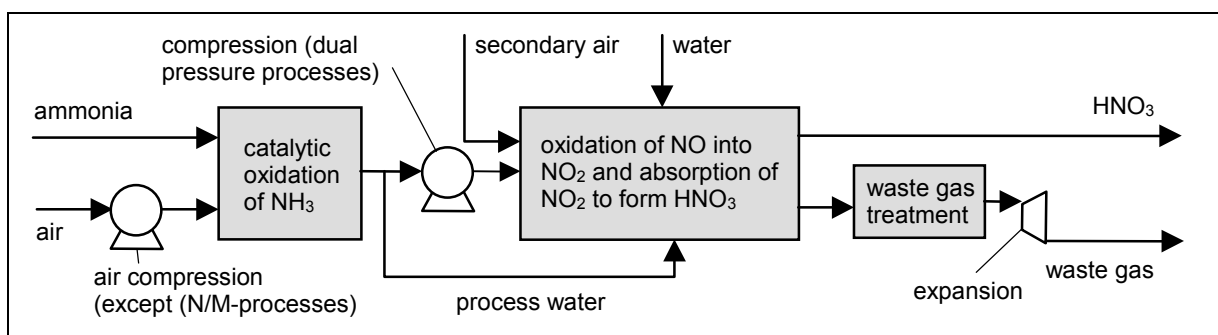


Figure 2: Simplified schematic representation of weak nitric acid production

At a concentration of 69.2 %, nitric acid forms an azeotropic composition with water. The production of **concentrated nitric acid** by distillation of weak nitric acid is not possible. Processes for the production of concentrated nitric acid are different from those for the production of weak nitric acid. Direct and indirect processes are in operation.



## 2.1 Input/Output

### 2.1.1 Ammonia

For the production of 1 t of  $\text{HNO}_3$  (100%), about 280 to 290 kg of ammonia are required, depending on the process technology. Frequently, a preceding ammonia plant supplies ammonia for the production of nitric acid.

Ammonia is mainly produced by steam reforming of hydrocarbons, with natural gas being the most common feedstock. By way of steam reforming processes the feedstock is reformed with steam in a heated primary reformer and subsequently with air in a secondary reformer, to produce synthesis gas ( $\text{N}_2$ ,  $\text{H}_2$ ), which also contains  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . After removal of  $\text{H}_2\text{O}$  (condensation),  $\text{CO}$  (methanation) and  $\text{CO}_2$  (chemical or physical absorption), the synthesis gas is compressed and synthesis of ammonia takes place on an iron catalyst.

Essential environmental parameters in the production of ammonia are the amount of feedstock needed, the consumption of energy for heating the primary reformer and the existence of an efficient heat recovery system. Further parameters relevant to the environment are waste gas emissions from the primary reformer, such as  $\text{CO}_2$ ,  $\text{NO}_x$ , and to some extent  $\text{NH}_3$  ( $\text{NO}_x$  abatement technology),  $\text{SO}_2$  and dust (depending on the fuel). Waste gas emissions are also caused by the removal of carbon dioxide ( $\text{CH}_4$ ,  $\text{CO}$  and  $\text{CO}_2$ ) and by the removal of purge gases from the synthesis loop ( $\text{NH}_3$  and  $\text{CH}_4$ ). Process water is removed from the synthesis gas by condensation and discharged; here an efficient wastewater treatment (recovery of ammonia by stripping processes) is state-of-the-art technology. Wastes arise from used catalysts and hydraulic fluids.

### 2.1.2 Air

Total air consumption for the production of 1 t of  $\text{HNO}_3$  (100%) is about 3,600 to 3,800  $\text{Nm}^3$ . With medium and high-pressure ammonia oxidation processes, about 10 to 20 % of the total air amount are provided as secondary air. The ratio of secondary to primary air declines with the pressure level. When N/M processes are used, about 30 % of air is provided as secondary air.

With production of concentrated nitric acid, liquid air is provided for the reaction of  $\text{N}_2\text{O}_4$  into  $\text{HNO}_3$ .

### 2.1.3 Water

About 1.93 t  $\text{H}_2\text{O}/\text{t N}$  is formed at the oxidation of ammonia. Process condensates already contain 2–45 %  $\text{HNO}_3$ , depending on the pressure of oxidation. Water is condensed by cooling downstream the ammonia oxidation and separated from the combustion gases.

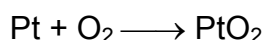
At the production of weak nitric acid, process condensates resulting from the ammonia combustion process are fully supplied into the absorption column. In addition, demineralised water provided from steam condensates is used for the absorption process. In addition to the process condensates, about 0.20  $\text{m}^3 \text{H}_2\text{O}/\text{t HNO}_3$  is required for the production of weak nitric acid with a concentration of 59.6 % [AGROLINZ 1999].

At the production of concentrated nitric acid, more process condensates are formed by ammonia oxidation than required. Part of the process condensate is discharged as wastewater.

### 2.1.4 Catalysts

Catalysts used for ammonia combustion usually consist of 90–95 % platinum and 5–10 % rhodium. The catalyst is woven to fine-meshed gauze. Several catalyst layers are installed at the ammonia combustion reactor. The number of catalyst layers increase with the pressure of ammonia combustion.

Catalysts are spent during the production of nitric acid due to precious metal losses. Precious metal loss is caused by vaporisation and mechanical losses. Mechanical losses typically account for about 20–25 % of the total loss [JOHNSON MATTHEW 2000]. Platinum loss due to vaporisation is thought to involve the formation of short-live platinum dioxide [THIEMANN, 1991].



Precious metal loss increases with temperature and gas flow rate which again increases with pressure. Loss of platinum is higher than loss of rhodium. Figure 3 presents the loss of precious metal at the catalytic ammonia oxidation as a function of temperature and catalyst composition.

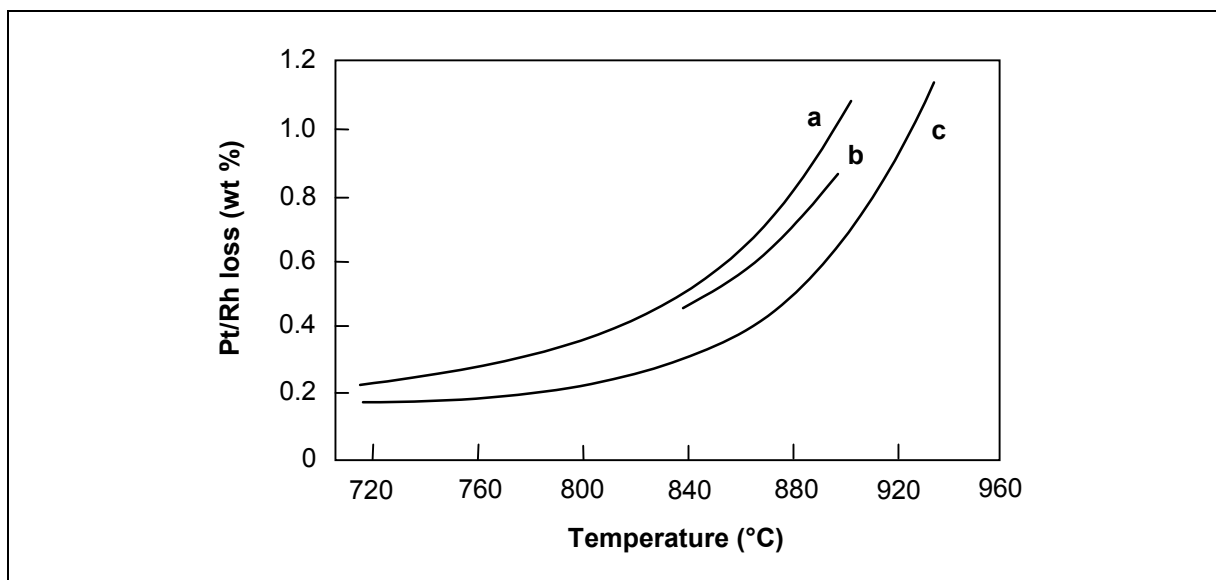


Figure 3: Loss of precious metal at the catalytic ammonia oxidation as a function of temperature and catalyst composition according to [THIEMANN et al. 1991]  
a) Pt; b) Pt-Rh 98/2; c) Pt-Rh 90/10

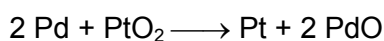
Particularly in plants with ammonia oxidation at medium or high pressures, a considerable loss of precious metal occurs. At a platinum loss of about 20 to 40% of the total amount, catalysts are exchanged [JOHNSON MATTHEW, 2000]. Working periods mainly depend on the catalyst loss. Table 1 presents operation parameters of  $\text{NH}_3$  oxidation (such as catalyst loss and working period) depending of the pressure of  $\text{NH}_3$  oxidation.

Table 1: Parameters of ammonia oxidation depending on the pressure of ammonia oxidation according to [ULRICHS 1981; THIEMANN et al. 1991, EFMA 1995; ENVIROCHEM 2000]

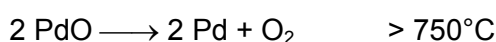
Pressure of NH <sub>3</sub> oxidation [bar]	Catalyst layer	Gas velocity [m/s]	Temperature [°C]	catalyst loss [g/ t HNO <sub>3</sub> ]	Working period [months]
1 bar	3–5	0.4–1.0	840–850	0.04–0.06	8–12
3–7 bar	6–10	1–3	850–900	0.10–0.16	4–7
8–12 bar	20–50	2–4	900–950	0.25–0.32	1.5–3

**Recovery of lost platinum** is achieved with palladium-based recovery systems. Mechanical filters were used for precious metal recovery before the development of palladium-based recovery systems.

Palladium-based **recovery systems** consist of gauzes made from pure palladium or an alloy containing 95% palladium and nickel. Platinum oxide (PtO<sub>2</sub>) that is lost from the catalyst gauzes is reduced to platinum metal and deposited on the surface of the palladium gauze. The captured platinum diffuses into the palladium gauze and alloys with the palladium, forming a solid solution.



Palladium oxidises at temperatures below 750°C and decomposes back to palladium at higher temperatures [JOHNSON MATTHEW 2000].



Design and number of gauzes depend on metal loss, production, campaign length and operating temperatures. More than 80 % of platinum and up to 30 % of rhodium can be recovered by palladium-based recovery systems. Precious metals which are not recovered precipitate on cold installation parts or can be found as deposit in the acid tank [JOHNSON MATTHEW 2000, THIEMANN et al. 1991].

**Mechanical filters** for recovery of precious metals are made of rock wool or glass wool. Recovery rates of 50 % have been reported. These mechanical filters show high pressure drops and are responsible for high energy losses. In particular in plants with low or medium pressure ammonia oxidation mechanical filters are not used any longer.

## 2.2 Products

Nitric acid is commercially available in two forms: weak nitric acid (< 69.2% HNO<sub>3</sub>) and concentrated nitric acid (> 95 % HNO<sub>3</sub>).

**Weak nitric acid** is used by the fertiliser industry to produce fertilisers on the basis of ammonium nitrate, NPK fertilisers, calcium ammonium nitrate and urea ammonium nitrate. Weak nitric acid is also used for production of adipic acid which itself is a starting material for nylon and polyester production.

**Concentrated nitric acid** is produced by indirect processes (concentrating weak nitric acid) or by direct processes. Concentrated acid is produced with concentrations up to 98 % HNO<sub>3</sub> and used for the production of nitric acid esters and nitro-aromatic compounds. These substances are used for production of explosive substances, nitro-cellulose lacquer, polyurethane, dyes and insecticides. Part of nitric acid is used for metallurgical applications.

## 2.3 Production of Weak Nitric Acid

### 2.3.1 Catalytic Combustion of Ammonia

Ammonia is vaporised in an evaporator. Water, hydraulic oils and other impurities deactivating catalyst are removed. Removed oil and water, containing high amounts of ammonia, are drained by gravity to a secondary ammonia vaporiser, where remaining ammonia is stripped. Evaporated ammonia is superheated with waste heat of secondary air compression and filtered in order to remove any rust from carbon steel equipment.

Air is filtered in a multistage filter system in order to remove particles and is subsequently compressed with an air compressor to the working pressure of ammonia combustion. At N/M plants, ammonia combustion takes place at a slight negative pressure. Air compressors are not required for this process.

Ammonia and primary air are mixed in a multistage static mixer and the NH<sub>3</sub>/air-mixture is filtered in order to get a homogenous gas flow and to avoid local ammonia excesses. The stoichiometric gas composition is approximately 14 vol. % of ammonia in air. However, this composition is in the explosive range of ammonia-air mixtures and it is normal to operate at lower levels. As the explosive limit falls with pressure, high-pressure plants usually do not work with ammonia concentrations exceeding 11 vol. %, whereas plants combusting ammonia under atmospheric pressure may operate at 13.5 vol. % [JOHNSON MATTHEY, 2000].

The exothermic ammonia oxidation takes place in a catalytic reactor.



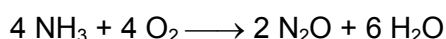
Catalysts consisting of 90–95 % platinum and 5–10 % rhodium are provided in form of gauze at the upper region of the reactor. Systems to recover precious metal losses are located below the oxidation catalyst.

The yield of ammonia oxidation mainly depends on pressure and temperature. Table 2 presents typical NH<sub>3</sub> inlet concentrations, combustion temperatures and yields of catalytic ammonia combustion for different pressure levels.

Table 2: Typical parameter for the catalytic ammonia combustion [EFMA 1995, THIEMANN et al. 1991]

Pressure of NH <sub>3</sub> combustion	NH <sub>3</sub> concentration [Vol. %]	Temperature [°C]	yield of NO [%]
1–2 bar	< 13.5	840–850	97–98
3–7 bar	< 11.0	850–900	96–96.5
> 8 bar	< 11.0	900–950	95

The yield of ammonia oxidation is declining with pressure and is further dependent on flow rate and combustion temperature of the gas compound. Consumption of ammonia and emissions of nitrous oxide (N<sub>2</sub>O) are dependent on the yield, as secondary reactions of ammonia burning are the conversion of NH<sub>3</sub> into N<sub>2</sub>O or nitrogen.



Heat arising from ammonia combustion is recovered in a waste heat boiler, located below the burners of the catalytic reactor. In the waste heat boiler steam is produced, which is used for the actuation of the compressor(s) and/or exported.

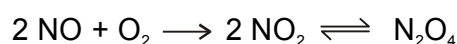
A set of gas/gas heat exchangers transfers energy from the gas leaving the waste heat boiler to the waste gas leaving the absorption column. In a cooling and condensing system following the heat exchangers, process gas is cooled to 20 °C. Thereby, process water is condensed and separated from the reaction gases. Finally, part of the NO oxidises into NO<sub>2</sub> during cooling. Depending on working pressure of ammonia combustion process water contains 2–40 % HNO<sub>3</sub>. Process water arising from weak nitric acid production is completely supplied into the absorption column.

At dual pressure plants, the NO<sub>x</sub> containing reaction gases are compressed with a nitrous gas compressor downstream cooling and separating the condensates. At single pressure plants, nitrous gas compression is not required, as catalytic oxidation of ammonia and absorption of nitrous gas take place at the same pressure.

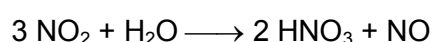
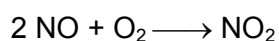
### 2.3.2 Oxidation and Absorption of Nitrogen Oxides

Oxidation of residual NO into NO<sub>2</sub> and absorption of NO<sub>2</sub> are performed in an absorption column. The oxidation of NO and the absorption of NO<sub>2</sub> are favoured by high pressures and low temperatures.

Secondary air is used in order to ensure a further conversion of NO into NO<sub>2</sub>. Secondary air is cooled after air compression in the ammonia superheater, thereby superheating ammonia input. Secondary air is conducted through an air bleacher for stripping dissolved NO<sub>x</sub> from raw nitric acid. Air loaded with NO<sub>x</sub> is added to the nitrous gas before it enters the absorption column. Oxidation of residual NO into NO<sub>2</sub> (or its dimer N<sub>2</sub>O<sub>4</sub>) occurs in the gas phase of the absorption column.



Complex reactions occur at the formation of nitric acid. On a whole, nitric acid is generated by absorption of nitrogen dioxide and dinitrogen tetroxide in water. By reaction of NO<sub>2</sub> with water, nitrogen monoxide is reformed, which prevents complete absorption of the inlet gases. The following overall reactions could be supposed for absorption and oxidation which take place at the absorption column:



Absorption columns are equipped with sieve plates which are cooled with inside water-cooled cooling coils in order to remove heat of reaction. Oxidation of NO into NO<sub>2</sub> proceeds rather slowly when the NO<sub>x</sub> concentration is low. Thus, spacing between the sieve plates increase with falling NO<sub>x</sub> concentration. Waste heat particularly arises from the formation of acid and has to be eliminated in order to get high absorption yields.

In the absorption column, process water is provided from the column head. Process condensate which has been separated from the reaction gases of ammonia oxidation is delivered to the sieve plate showing the appropriate acid concentration.

Absorption efficiency is an essential parameter for NO<sub>x</sub> concentration of the waste gas exiting the absorption column. Altogether, absorption efficiency depends on absorption pressure, cooling efficiency at the absorption column and on the design of the absorption column (absorption volume and number of sieve plates). High absorption efficiencies are achieved in particular with high absorption pressures (e.g. 15 bar).

The waste gas leaves the absorption column with a temperature of about 20–30 °C and is heated in several steps with waste heat, which is mainly recovered from the nitrous gas stream leaving the waste heat boiler. In most of the nitric acid plants, waste gas is subjected to processes for reduction of NO<sub>x</sub> emissions (cf. chapter 3.4.1). Finally, waste gas is expanded in a waste gas turbine.

### 2.3.3 Process Technology of Weak Nitric Acid Production

The main unit operations involved in the nitric acid process are the same for all types of plants. In sequential order these are [EFMA 1995, THIEMANN et al. 1991]:

- Air filtration
- Air compression (with exception of N/M dual pressure plants)
- Air/ammonia mixing
- Air/ammonia oxidation over catalytic gauze
- Energy recovery by steam generation and/or gas re-heating
- Gas cooling
- Gas compression, energy recovery and cooling (dual pressure plants only)
- Absorption, with the production of nitric acid
- Heating of waste gas leaving absorption
- Abatement of NO<sub>x</sub> emission (e.g. SCR process)
- Energy recovery by expansion of the waste gas to atmosphere, in a gas turbine.

Due to different thermodynamic conditions for ammonia combustion and absorption, process technologies differ with regard to working pressure levels.

#### 2.3.3.1 Single Pressure Plants

At single pressure plants, oxidation of ammonia is performed at the same pressure level as absorption. M/M- and H/H single pressure plants are in operation. At these plants nitrous gas compression is not required. For the compression to high pressures, two-stage compressors are used. Characteristic features of single pressure plants are:

- In **single pressure plants**, ammonia consumption level is higher than in dual pressure plants, as the overall yield is lower. Single pressure plants show lower construction expenses, but higher operating costs in relation to dual pressure plants.
- At **H/H single pressure plants**, oxidation of ammonia occurs at a rather unfavourable (high) pressure level with regard to ammonia oxidation yield. Consumption of ammonia increases with higher oxidation pressures and a substantial part of ammonia reacts into N<sub>2</sub> and N<sub>2</sub>O. H/H single pressure plants show rather high N<sub>2</sub>O emission levels. Loss of catalyst is high; thus working periods are short. H/H plants are characterised by high absorption efficiencies due to high absorption pressures.
- At **M/M single pressure plants**, oxidation of ammonia occurs at a more favourable pressure. M/M single pressure plants show lower N<sub>2</sub>O emission than H/H single pressure plants. Absorption efficiency is rather low due to an unfavourable (low) absorption pressure level. Consumption of ammonia is high, due to absorption losses resulting in high NO<sub>x</sub> concentrations in the waste gas leaving the absorption column. NO<sub>x</sub> reduction of the waste gas with an SCR reactor requires a considerable amount of ammonia as reducing agent.
- **Plants with atmospheric pressure absorption (N/N plants) do not correspond to state-of-the-art technology.**

Figure 4 presents a simplified schematic representation of a single pressure nitric acid plant.

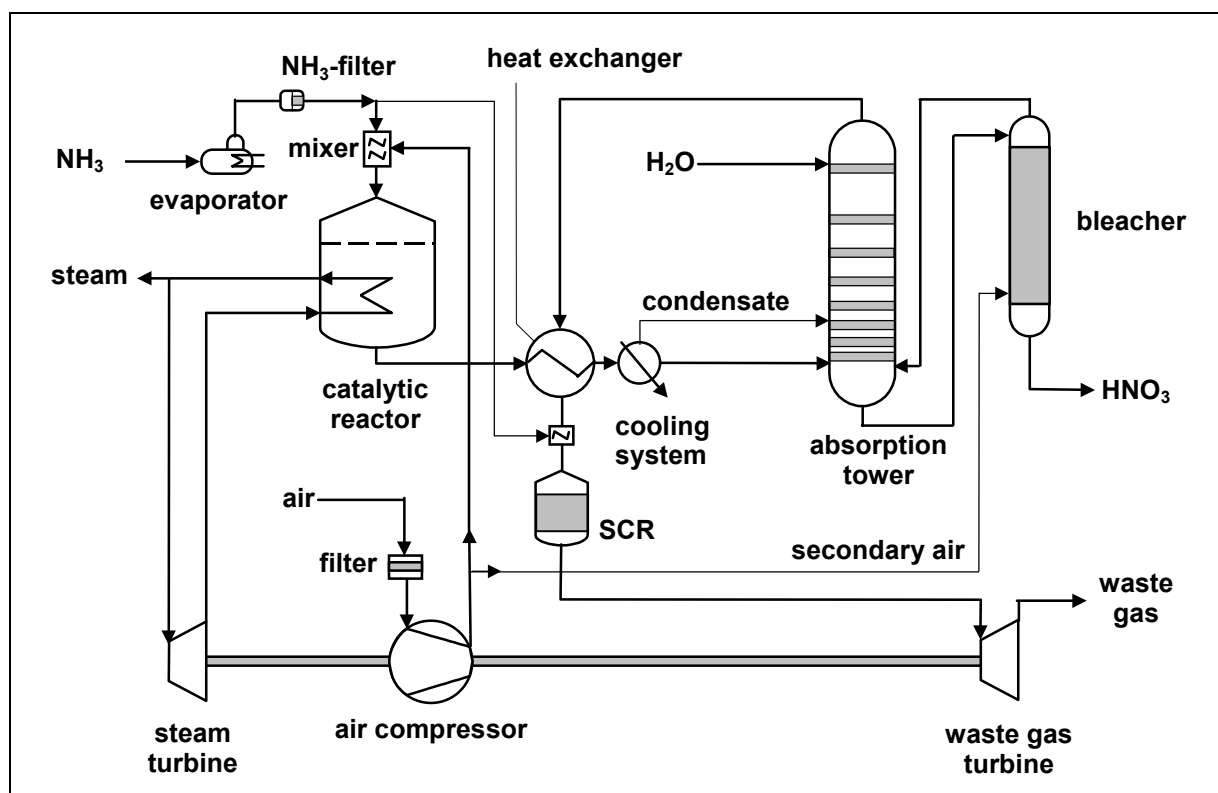


Figure 4: Simplified schematic representation of a single pressure nitric acid plant

### 2.3.3.2 Dual Pressure Plants

With dual pressure plants, working pressure of absorption is higher than pressure of catalytic ammonia oxidation. A nitrous gas compressor boosts the pressure from the front end of the process (ammonia oxidation) to the back end (absorption). Characteristic features of dual pressure plants are:

- In **dual pressure plants**, the relation of nitric acid output to ammonia input is higher than in single pressure plants. With dual pressure plants, higher investment expenses (compared to single pressure plants) are opposed to lower operating expenses.
- **M/H dual pressure plants** work with ammonia oxidation at medium pressure and with absorption at high pressure. Ammonia combustion occurs at a more favourable pressure compared to H/H single pressure plants. Absorption of nitrogen dioxide occurs at high pressure in order to increase the absorption efficiency. Loss of precious metal is recovered with recovery systems. New plants tend to be designed with pressure levels above atmospheric pressure for the oxidation of ammonia to nitric oxide, due to lower gas volumes and lower investment expenses; thus new dual pressure plants are as a rule designed as M/H plants.
- **N/M dual pressure plants** operate with ammonia oxidation at atmospheric (normal) pressure and with absorption at medium pressure. In relation to M/M single pressure plants, ammonia combustion takes place at a more favourable pressure. This results in higher  $\text{NH}_3$  conversion rates and in a lower  $\text{N}_2\text{O}$  emission level. Platinum recovery systems are rarely in operation, as they show high pressure drops in relation to the pressure of ammonia oxidation. With N/M processes, loss of precious metal without recovery is comparable to net precious metal loss at M/H processes with recovery systems. Combustion of ammonia at atmospheric pressure requires large gas volumes and higher investment expenses. Thus, new plants are not constructed as N/M plants any longer.

Figure 5 is a simplified schematic representation of a dual pressure nitric acid plant.

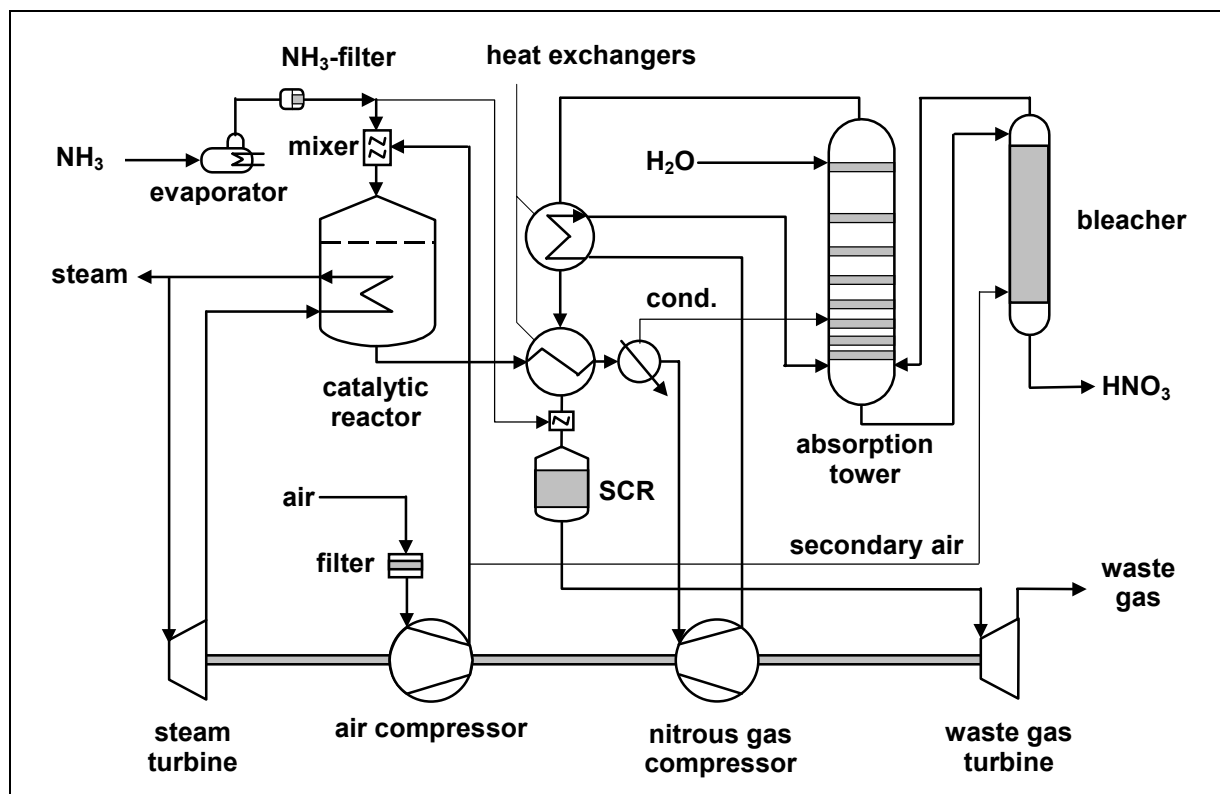


Figure 5: Simplified schematic representation of a M/H dual pressure nitric acid plant

Table 3 is a comparison of different plant technologies for the production of weak nitric acid. With regard to ammonia input, run time, platinum loss and cooling water amount, the M/H process is the most efficient plant design. High-pressure steam export of M/H plants is between M/M and H/H plant.

Table 3: Typical consumption figures for steam-turbine-driven nitric acid plants per metric ton  $\text{HNO}_3$  (100 %) and tail gas containing < 50 ppm  $\text{NO}_x$ , according to [KRUPP, 2001]

	single pressure plant		dual pressure plant
	M/M	H/H	M/H
operating pressure [bar]	6	10	4.6/12
Ammonia [kg]	286	290	283
Electric Power [kWh]	9	13	8.5
Platinum primary losses [g]	0.15	0.26	0.13
LP heating steam, 8 bar, saturated [t]	0.05	0.35	0.05
HP excess steam, 40 bar, 450 ° C [t]	0.75	0.58	0.65
cooling water <sup>1)</sup> [t]	100	125	105

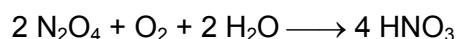
<sup>1)</sup> Delta T = 10 K, including water for steam turbine condenser



## 2.4 Processes for the Production of Concentrated Nitric Acid

Information on emission and consumption levels for the production of highly concentrated nitric acid are not available in Austria, as the production of concentrated nitric acid was ceased quite some time ago.

**Direct processes** for the production of concentrated nitric acid are based on the production of liquid  $\text{N}_2\text{O}_4$ , which reacts under pressure with oxygen and dilute nitric acid to form  $\text{HNO}_3$ .



Nitrogen oxides, which are formed in a ammonia combustion unit operated at low pressure, are completely oxidised into  $\text{NO}_2$  (oxidation step and post-oxidation step).  $\text{NO}_2$  is washed out with concentrated nitric acid (absorption step) and by process condensate and dilute nitric acid (final absorber step).  $\text{NO}_2$  (or its dimer  $\text{N}_2\text{O}_4$ ) is stripped from the concentrated acid (bleaching) and liquefied. Concentrated acid is formed from liquid  $\text{N}_2\text{O}_4$ , oxygen and dilute nitric acid (from final absorption step) in a reactor at a pressure of about 50 bar. Concentrated nitric acid is recirculated to the absorption and final oxidation steps, part of nitric acid is withdrawn as product acid.

Waste gas is discharged from the final absorption step.  $\text{NO}_x$  concentration of the waste gas depends on the temperature of the final absorption step. Process condensates and dilute nitric acid arising from catalytic ammonia oxidation, oxidation and postoxidation step are re-used. However, more process condensate is formed than can be used for production of concentrated acid. Part of the process condensates has to be used for other production or treated as wastewater.

**Indirect processes** are based on extractive distillation and rectification of weak nitric acid. Sulphuric acid or magnesium nitrate is used as dehydrating agent.

With sulphur acid processes, weak nitric acid is preheated and distilled with  $\text{H}_2\text{SO}_4$ . With magnesium nitrate processes, a solution of  $\text{MgNO}_3$  is used to extract water from the nitric acid. Dehydrating agents are restored under vacuum. Process condensates which demand an adequate wastewater treatment arise from concentrating the dehydrating agent. Vapour withdrawn from the head of the distillation or extraction column is condensed to form concentrated nitric acid. Waste gases contain nitric acid vapour and are scrubbed with dilute nitric acid.

## 2.5 Energy

Reactions taking place at nitric acid production are exothermic to a great extent. According to [KONGSHAUG 1998] the reaction from ammonia to 60 % nitric acid theoretically releases 28.5 GJ/t N- $\text{HNO}_3$  corresponding to about 6.3 GJ/t  $\text{HNO}_3$  (100 %). Beside the production of nitric acid also steam or mechanical energy is produced by a nitric acid plant.

Nitric acid production according to state-of-the-art technology is characterised by a high degree of energy regeneration. A modern nitric acid plant with dual pressure process has a net energy export of 11 GJ/t  $\text{HNO}_3$ -N as high-pressure steam [KONGSHAUG 1998], corresponding to about 2.4 GJ/t  $\text{HNO}_3$  (100 %). The average net energy export for Europe is assumed at 7 GJ/ t N [KONGSHAUG 1998], corresponding to about 1.6 GJ/ t  $\text{HNO}_3$ .

- **Production of high-pressure steam**

The highly exothermic catalytic conversion of ammonia takes place in the **catalytic reactor** at temperatures between 840 and 950 °C. Waste heat arising from ammonia oxidation is recovered in a **waste heat boiler** arranged below the ammonia burners and used for

high-pressure steam production. Part of the high-pressure steam produced in the waste heat boiler is used for supply of the compression energy (mechanically or electrically). Excess is exported as product steam.

- **Recovery of low level energy**

A set of **gas/gas heat exchangers** recover low level energy from the nitrous gases leaving the waste heat boiler. The energy is transferred to the waste gas leaving the absorption column. Waste heat arising from the nitrous gas compression (dual pressure plant) can be used for preheating the waste gas leaving the absorption column, as well. Reheating of the waste gas is accomplished for an adiabatic operation of the waste gas expansion turbine and enables operation of a selective catalytic reduction (SCR) process without requirement of additional heating to the SCR working temperature.

Waste heat arising from the compression of secondary air is used in an **ammonia super-heater** for preheating ammonia, thereby cooling the secondary air. Low level energy of the nitrous gas stream can also be used for preheating primary air and for preheating boiler feedwater. Low-pressure steam (e.g. from electric power generation) can be used for evaporating or stripping ammonia (**ammonia evaporator**) and for deaeration of boiler feedwater.

- **Supply of the compression energy**

Drive power for compressors (**air compressor** and/or **nitrous gas compressor**) is usually supplied by a **waste gas expansion turbine** and a **steam turbine**, which are coupled mechanically to the compressors. The waste gas expansion turbine recovers part of the compression energy, depending on the degree of preheating of the cold waste gas downstream the absorption step. Remaining drive power required is usually provided by the steam turbine running on process steam. If the process steam is completely exported (e.g. for electric power generation), instead of the steam turbine, an **electric motor drive** is used for the actuation of the compressors.

- **Cooling water demand**

In a **cooler condenser**, the nitrous gas stream is cooled down with cooling water to temperatures of 20–30 °C, so that water formed during ammonia oxidation condenses. Reaction heat released in the **absorption column** has to be carried off by cooling water, as both the oxidation of NO into NO<sub>2</sub> and the absorption of NO<sub>2</sub> are favoured by low temperatures. Part of the heat absorbed by the cooling water can be used for evaporating ammonia [ENVIROCHEM, 2000].

In table 4, energy input and output of nitric acid plants at Linz are given. Specific energy input for compression is given for steam actuation and for actuation with electric energy.

Table 4: Energy input and output of the nitric acid plants at Linz [AGROLINZ 1999]

	Line E M/H process	line F N/M process
<b>energy consumption for compression</b>		
compression with electric actuation [MWh/h]	~ 5	
compression with steam actuation [t steam/h]		~ 20 <sup>2)</sup>
<b>energy consumption except compression [MWh/h]</b>	~ 0.55	~ 0.60
<b>steam production [t steam/h]</b>	~ 43 <sup>1)</sup>	~ 25 <sup>2)</sup>

<sup>1)</sup> 42 bar / 520°C

<sup>2)</sup> 23 bar / 350°C

## 2.6 Storage

**Ammonia** is stored either in liquid state in storage tanks at temperatures of  $-33^{\circ}\text{C}$  or under pressure in pressure tanks.

For storing of liquid refrigerated ammonia, insulated cylindrical tanks with fixed roofs and flat bottoms are used. Storage tanks consist of two walls of low-temperature steel. The storage tanks must be safeguarded against high pressures and are equipped with shut-off valves, safety relief valves and with recompression installations to liquefy the boil-off. Storage tanks for compensation of production and consumption with a storage capacity equivalent to about 20 days are common [EFMA 1995, BAKEMAIER et al. 1986]. Pressure storage systems are used for smaller ammonia quantities. Spherical vessels (< 1500 t) and cylindrical tanks (< 150 t) are used.

**Nitric acid** is stored in tanks made of stainless steel or at concentrations of more than 95 % in tanks made of aluminium alloy. Tanks should be designed for at least a slight pressure and vacuum. This design will permit the venting of nitrogen oxide fumes to collection and disposal equipment [GROSSEL 2000].

### 3 AIR EMISSIONS AND EMISSION REDUCTION

Nitrogen oxides (NO<sub>x</sub>) and nitrous oxides (N<sub>2</sub>O) are major air emissions of nitric acid production. Waste gas volume varies for different process technologies (dependent on ammonia input, secondary air input, yields of the ammonia oxidation step and the absorption step) between 3,130–3,300 Nm<sup>3</sup>/t HNO<sub>3</sub> [EFMA 1995].

#### 3.1 Emissions of Nitrogen Oxides (NO<sub>x</sub>)

At the production of weak nitric acid, the absorption step is essential for NO<sub>x</sub> concentration of the waste gas. Crucial parameters for a high absorption efficiency resulting in low NO<sub>x</sub> emission level are [VDI 1983; THIEMANN et al. 1991]:

- Pressure: High absorption pressure favours high absorption efficiency and low NO<sub>x</sub> emission level. Absorption yield in modern plants with high pressure absorption columns is above 99,8 % [GRY, 1994].
- Temperature: Low absorption temperature favours high absorption efficiency;
- Reaction volume;
- Low solubility of the nitrogen monoxide in water or nitric acid;
- Partial pressures of nitrogen oxides and oxygen: Compared to waste gases of other industrial processes, molar rate of NO<sub>2</sub>/NO in waste gas of a nitric acid plant is rather high. High NO<sub>2</sub> contents in the waste gas results in a red brown colour of the waste gas. In addition to the given emission limit (< 200 ppm), [TA Luft 1986] requires, that the NO<sub>2</sub> concentration be kept below the following equation, in order to avoid a red-brown colour of the waste gas:

$$\text{mass concentration of NO}_2 \text{ [mg/Nm}^3\text{]} = \frac{1200}{\text{inside diameter of stack orifice (dm)}}$$

With the application of high absorption pressures (about 15 bar), waste gas might have considerable low NO<sub>x</sub> contents (cf. chapter 3.4.3). In this case, end-of-pipe technologies for emission reduction are not applied.

For achieving low NO<sub>x</sub> emission levels, most nitric acid plants are equipped with end-of-pipe technologies. Among end-of-pipe measures, the selective catalytic reduction (SCR) process can be considered state-of-the-art technology for the reduction of NO<sub>x</sub> emissions (cf. chapter 3.4.1).

By application of NSCR techniques (cf. chapter 3.4.1) for reduction of NO<sub>x</sub> emissions at nitric acid plants, cross media effects such as high secondary emissions of CO, HCN, CO<sub>2</sub> and VOC and high levels of fuel consumption have to be considered. For that reason, the NSCR process cannot be considered state-of-the-art technology for nitric acid production.

Table 5 presents NO<sub>x</sub> emission levels of the Austrian nitric acid plants and relevant operating parameters of the absorption processes. These plants are equipped with SCR installations for reduction of NO<sub>x</sub> emissions. NO<sub>x</sub> concentrations are given for the waste gas leaving the absorption column (before the SCR reactor) and the waste gas downstream the SCR installation.

Table 5: NO<sub>x</sub> emissions and operation parameter relating to the absorption at the Austrian nitric acid plants [AGROLINZ, 1999].

	line E M/H process	line F N/M process
pressure for absorption (pressure above atmospheric)	8 bar	3.8 bar
absorption temperature	25 °C	25 °C
absorption efficiency	99.6 %	98.2 %
NO <sub>x</sub> concentration before SCR reactor [ppm]	≤ 500 ppm	2,000–3,000 ppm
NO <sub>x</sub> concentration after SCR reactor [ppm] [mg NO <sub>x</sub> /Nm <sup>3</sup> ] <sup>1)</sup> [kg NO <sub>x</sub> /t HNO <sub>3</sub> ] <sup>1) 2)</sup>	ca. 90 ppm 180–190 mg/Nm <sup>3</sup> 0.54–0.56 kg/t HNO <sub>3</sub>	ca. 155–160 ppm 320–330 mg/Nm <sup>3</sup> 0.98–0.99 kg/t HNO <sub>3</sub>

<sup>1)</sup> as NO<sub>2</sub>

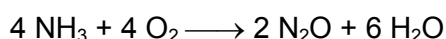
<sup>2)</sup> specific emissions referred to 100 % HNO<sub>3</sub>

At processes for production of concentrated nitric acid NO<sub>x</sub> concentration of the waste gas (apart from application of NO<sub>x</sub> abatement) depends on temperature of the final absorption step [VDI 1983]. Specific NO<sub>x</sub> emissions of concentrated acid processes are reported with 0.1 to 1 kg/t HNO<sub>3</sub> (100 %), based on data of French and German plants [CITEPA, 1992].

### 3.2 Emissions of Nitrous Oxides (N<sub>2</sub>O)

Nitrous oxide (N<sub>2</sub>O) is a greenhouse gas with a greenhouse potential of about 310 times as high as CO<sub>2</sub> over a 100 year time horizon. Major polluters contributing to the N<sub>2</sub>O emissions are agriculture, the energy sector (traffic and combustion processes) and industrial processes. Here, the production of adipic acid and nitric acid are the most relevant industrial processes. Processes for the reduction of N<sub>2</sub>O have successfully been installed at adipic acid plants and have already led to a significant reduction of N<sub>2</sub>O emissions [KÜHN, 2001]. Austrian nitric acid plants are the major industrial polluters contributing to N<sub>2</sub>O emissions. Production of adipic acid does not exist in Austria.

Nitrous oxide forms at the catalytic oxidation of ammonia. Ammonia reacts into NO; here, efficiencies of 93 and 98 % are achieved. The conversion efficiency of ammonia to nitric oxide is a function of temperature, pressure, velocity of gas stream, volume of catalyst, and purity of the ammonia and air streams. Residual ammonia (2–7 %) reacts in secondary reactions into nitrogen N<sub>2</sub> and at least partly into nitrous oxide (N<sub>2</sub>O).



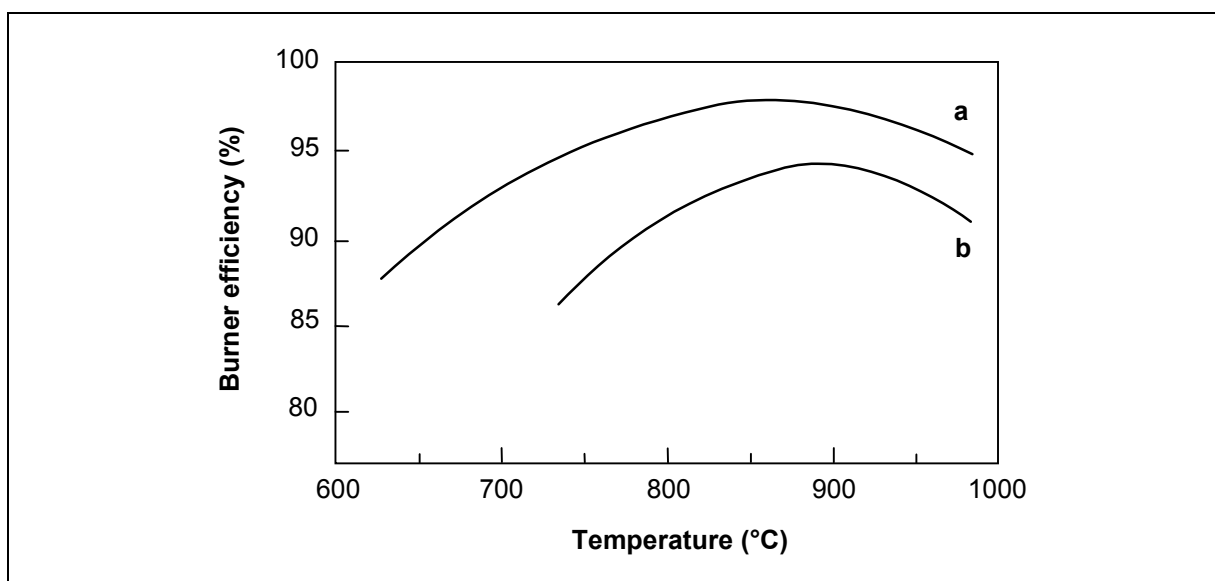


Figure 6: Efficiency of catalytic ammonia oxidation as functions of temperature and pressure according to [THIEMANN et al. 1991]; a) 1 bar; b) 4 bar

Table 6 presents  $N_2O$  emission levels of the Austrian nitric acid plants and relevant operating parameters of the catalytic ammonia oxidation.

Table 6:  $N_2O$  emissions and operation parameter relating to catalytic ammonia combustion of the Austrian nitric acid plants [AGROLINZ, 1999].

	line E M/H process	Line F N/M process
pressure for catalytic ammonia combustion (pressure above atmospheric)	3.3 bar	- 0.08 bar
combustion temperature	895 °C	840–850 °C
efficiency of catalytic ammonia combustion	95 % <sup>1)</sup>	95 % <sup>1)</sup>
$N_2O$ -concentration in waste gas [ppm] [mg/Nm <sup>3</sup> ] [kg/t HNO <sub>3</sub> ] <sup>2)</sup>	1,000–1,400 ppm 1,960–2,750 mg/Nm <sup>3</sup> 5.8–8.1 kg/t HNO <sub>3</sub>	600–800 ppm 1,180–1,570 mg/Nm <sup>3</sup> 3.6–4.8 kg/t HNO <sub>3</sub>

<sup>1)</sup> calculated value; average yield of catalytic ammonia combustion for line E and line F

<sup>2)</sup> specific emissions related to 100 % HNO<sub>3</sub>

Considering the emission values presented above, annual  $N_2O$  emissions of the Austrian nitric acid plants can be estimated at about 2,400–3,500 t/a. With regard to the total  $N_2O$  emissions in Austria [RITTER et al. 2000],  $N_2O$  emissions from Austrian nitric acid plants can be estimated at about 25–30 % of the total  $N_2O$  emissions in Austria.

[ORTHOFFER et al. 1993] estimated nitrous oxide emissions from Austrian nitric acid plants at about 520 t/a (about 11% of the total  $N_2O$  emissions). They indicated emission factors of 0.6 kg  $N_2O$ /t HNO<sub>3</sub> (normal pressure NH<sub>3</sub> oxidation) and 1.5 kg  $N_2O$ /t HNO<sub>3</sub> (medium pressure ammonia oxidation). These emission factors are significantly lower than the emission factors presented in table 3.2. This discrepancy might be caused by analytical problems with the former single measurements. Nowadays,  $N_2O$  concentrations are measured continuously, which is the more reliable method [AGROLINZ 2000].

### 3.3 Other Air Emissions

#### 3.3.1 Diffuse Emissions

Diffuse emissions of  $\text{NH}_3$ ,  $\text{NO}_x$  or  $\text{HNO}_3$  are released during purging operations, and due to leakage of piping or sealing and leakage of compressors and turbines. In order to prevent diffuse emission from nitric acid storage, disposal equipment such as scrubbers can be installed. A recompression installation is provided at ammonia storage tanks to liquefy the ammonia boil-off.

#### 3.3.2 Emissions from Start-up and Shut-down Operations

Dependent on process technology, several start-up and shut-down operations have to be considered at nitric acid plants every year. Due to unstable process conditions, additional  $\text{NO}_x$  emissions are released in particular during start-up operations. Emission values of Austrian nitric acid plants are not known.

For the nitric acid plants at Linz, regulations exist for exceeding the emission limits which also apply to start-up and shut-down operations. If emission limits including start-up or shut-down operations are exceeded, the stipulated daily average limit of 50 kg  $\text{NO}_x/\text{h}$  has to be met within 24 hours after the incident. This period of time starts with the moment the emission limit was exceeded [FIERLINGER, 1999].

#### 3.3.3 Secondary Emissions

The application of non-selective catalytic reduction (NSCR) processes (cf. chapter 3.4.1) causes considerable secondary emissions of CO and VOC and even small amounts of HCN-emissions. VOC emissions of about 700–3,000 mg/ $\text{Nm}^3$  are reported. Total emissions of CO and VOC can amount to 0.4 vol. % [DITTMAR 1985].

Slight  $\text{NH}_3$  emissions may be caused by the use of selective catalytic reduction (SCR) processes (cf. chapter 3.4.1) due to slip of  $\text{NH}_3$ . However, with the use of modern catalysts, these emissions are below 5 ppm. At Austrian plants, ammonia slip from SCR processes is between 0.25 and 2.0 mg/ $\text{Nm}^3$  for line E (M/H process,  $\text{NO}_x$  concentration before SCR < 500 ppm) and between 0.05 and 0.10 mg/ $\text{Nm}^3$  for Line F (N/M process,  $\text{NO}_x$  concentration before SCR between 2,000 and 3,000 ppm) [AGROLINZ, 1999].

### 3.4 Reduction of $\text{NO}_x$ Emissions

$\text{NO}_x$  concentration after the absorption section mainly depends on the pressure applied at the absorption section. Low  $\text{NO}_x$  emissions can be achieved by high absorption efficiencies (e.g. application of high absorption pressures) and/or by end-of-pipe technologies. For reduction of  $\text{NO}_x$ -emissions most nitric acid plants are equipped with end-of-pipe technologies.

#### 3.4.1 End-of-pipe Processes for the Reduction of $\text{NO}_x$ Emissions

For reduction of  $\text{NO}_x$  emissions at nitric acid plants, catalytic end-of-pipe techniques are used. Here, selective catalytic reduction (SCR) and non-selective catalytic reduction (NSCR) are applied techniques.

Table 7 presents waste gas concentrations of NO<sub>x</sub> and N<sub>2</sub>O and other relevant parameters of waste gas at nitric acid plants downstream the absorption column and before end-of-pipe techniques for emission abatement.

Table 7: Parameters of waste gas from nitric acid plants downstream the absorption column before the application of end-of-pipe techniques for emission abatement according to [THIEMANN et al. 1991; BLANCO 1998]

Composition and conditions	HNO <sub>3</sub> plant
NO <sub>x</sub> (mg NO <sub>2</sub> /Nm <sup>3</sup> )	200–4,000 <sup>*)</sup>
NO/NO <sub>2</sub> (molar rate)	about 1/1
N <sub>2</sub> O (mg/Nm <sup>3</sup> )	600–3,000 <sup>**)</sup>
O <sub>2</sub> (% vol.)	1–4
H <sub>2</sub> O (% vol.)	0.3–0.7
Pressure (ATM)	3–12
Temperature downstream absorption (°C)	20–30
Temperature after reheating (°C)	200–500
Gas flow (Nm <sup>3</sup> /h)	(20–100) x 10 <sup>3</sup>

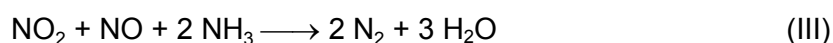
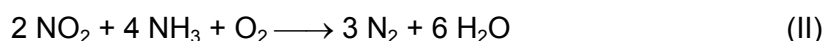
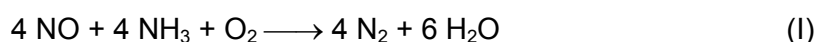
<sup>\*)</sup> NO<sub>x</sub> concentrations are presented for the waste gas downstream the absorption column and before emission reduction by end of pipe techniques; NO<sub>x</sub> concentrations vary for different absorption pressures

<sup>\*\*)</sup> N<sub>2</sub>O concentrations mainly depend on process conditions of the catalytic ammonia oxidation process.

### 3.4.1.1 Selective Catalytic Reduction (SCR Process)

Since the mid-seventies, selective catalytic reduction has been installed at nitric acid plants for NO<sub>x</sub> abatement.

At selective catalytic reduction processes, nitrogen oxides of the waste gas selectively react on a catalyst with ammonia which is provided as a reducing agent. NH<sub>3</sub> is absorbed at the catalyst and reacts with the oxygen of NO<sub>2</sub> and NO to give N<sub>2</sub> and H<sub>2</sub>O. The following overall reactions take place:



The SCR installation consists of an SCR reactor, piping for ammonia supply and a static gas mixer for mixing ammonia and waste gas. Storage equipment for ammonia is not required for an SCR installation at a nitric acid plant, as the ammonia is directly provided from the process. Figure 7 presents a simplified schematic representation of an SCR process installed at a nitric acid plant.

A small ammonia stream that feeds the SCR reactor goes through a similar evaporation process as the ammonia evaporation for nitric acid production. Ammonia is evaporated and superheated by low-pressure steam. The ammonia vapour stream is filtered before mixing with the waste gas stream for NO<sub>x</sub> abatement [ENVIRO-CHEM, 2000].



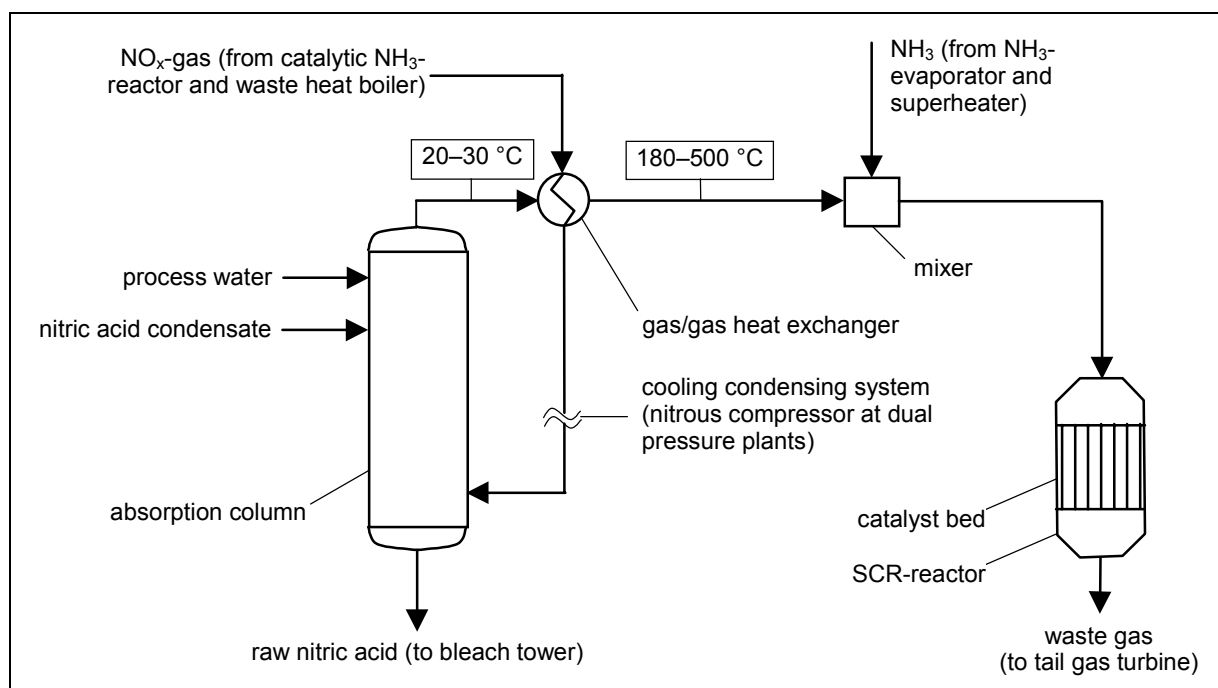


Figure 7: Simplified schematic representation of a selective catalytic reduction (SCR) process at a nitric acid plant

As the temperature of the waste gas leaving the absorption column is about 20–30 °C, waste gas has to be heated to the working temperature of the SCR reactor, which is between 180 and 500 °C. Heating of the waste gas takes place by heat displacement with gas/gas heat exchangers. Waste heat of the process gas downstream the waste heat boiler and optionally waste heat of the waste gas subsequent to the waste gas expansion turbine is used. Heat displacement is integrated in the process for nitric acid production and carried out for an adiabatic operation of the waste gas expansion turbine. Therefore, expenses for reheating of the waste gas cannot be added to the SCR process.

Before entering the SCR reactor, waste gas is mixed with ammonia. The gas mixture is supplied to the SCR reactor and flow through the catalyst. At the pores of the catalyst, ammonia reacts with nitrogen oxides  $\text{NO}_x$  to form  $\text{N}_2$  and  $\text{H}_2\text{O}$ .

Catalysts are composed of precious metals or of transition metal oxides (e.g.  $\text{V}_2\text{O}_5$ ,  $\text{TiO}_2$ ,  $\text{CuO}$  and  $\text{NiO}$ ) supported on alumina or titanium oxide. Structure of catalysts can be monolithic (honeycomb) or in particles, plates, cylinders or spheres. Different catalysts for different temperature ranges exist. The optimum temperature range varies with the type of catalyst used. According to [GRY 1994 and 2000] several SCR units have been installed, using zeolite catalysts. Conversion rates of about 95 %,  $\text{NO}_x$  emission levels of 100 mg  $\text{NO}_x/\text{Nm}^3$  (as  $\text{NO}_2$ ) and ammonia leakage below 0.2 mg  $\text{NH}_3/\text{Nm}^3$  are reported.

The SCR reactor can be installed upstream or downstream of the waste gas expansion turbine [CLARK 1998]. At an installation of the SCR process downstream to the waste gas expansion turbine, the SCR reactor is operated at atmospheric pressure, thus conventional SCR equipment can be used for  $\text{NO}_x$  abatement. Waste gas has to be reheated downstream the waste gas expansion turbine. Therefore a waste heat displacement system for energy recovery has to be installed downstream the SCR reactor. With an installation of the SCR process upstream the waste gas expansion turbine, the SCR reactor is operated at the pressure of the absorption column. Mechanical requirements of the reactor have to be met, due to higher pressure levels. Advantages are a smaller size of the SCR reactor and catalyst, and less influence of the pressure drop on the power delivered by the expansion turbine [GALINDO AND CORTÓN, 1998]. Additional expenses are not required for heat displacement.

**Characteristic features** of the SCR technique in nitric acid plants are:

- The SCR process allows conversion rates of up to 95 % at nitric acid plants. The SCR process shows a wide operative range. SCR installations with NO<sub>x</sub> inlet concentration up to 3,000 ppm are in operation.
- The SCR process shows high selectivity for reduction of NO<sub>x</sub>. Ammonia selectively reduces NO<sub>x</sub> without appreciable oxygen removal. The reducing agent is highly available, as ammonia can directly be taken from the input of the nitric acid plant.
- Catalysts are available for a wide temperature range. SCR catalysts are not exposed to high temperatures such as catalysts for the NSCR process. Lifetime of SCR catalysts is more than 10 years and significantly exceeds the lifetime of NSCR catalysts.
- Pressure drop has low influence on the power delivered by the expansion turbine, if the SCR reactor is installed upstream the waste gas expansion turbine.
- The use of SCR may cause slight NH<sub>3</sub> emissions due to the slip of ammonia. However, with application of modern catalysts ammonia slip is far below 5 ppm (3.8 mg/Nm<sup>3</sup>).
- Functional and operational reliability of SCR processes for NO<sub>x</sub> reduction at nitric acid plants is high. Since 1975 a large number of SCR reactors have been installed at nitric acid plants.

SCR can be considered state-of-the-art technology for new and existing plants. For new plants in particular a combination of SCR process and high-pressure absorption can be considered state-of-the-art technology. By application of SCR processes at plants with **high-pressure absorption** (< 8 bar), NO<sub>x</sub> emissions of **100–200 mg/Nm<sup>3</sup>** (as NO<sub>2</sub>) are achievable. By application of SCR processes at plants with **medium pressure absorption** (4–8 bar) NO<sub>x</sub> emissions of **200–350 mg NO<sub>x</sub>/Nm<sup>3</sup>** (as NO<sub>2</sub>) are achievable [AGROLINZ 1999, GRY 1994 and 2001, DITTMAR 1985].

**Reference plants:** AGROLINZ GmbH operates two nitric acid plants, referred to as line E and line F, for the production of weak nitric acid with a concentration of 59,6 % HNO<sub>3</sub>.

- Line E is a dual pressure plant (M/H process) and has a capacity of 300,000 t/a. Working pressures are 3.3 bar for ammonia oxidation and 8 bar for the absorption (pressures above atmospheric). In 1994, a supplementary SCR reactor has been installed in line E. The NO<sub>x</sub> concentration of the waste gas leaving the absorption column is < 500 ppm (< 1,000 mg NO<sub>x</sub>/Nm<sup>3</sup> as NO<sub>2</sub>). The NO<sub>x</sub> concentration of waste gas leaving the SCR reactor is about 180–190 mg/Nm<sup>3</sup>. Ammonia slip is between 0.26 and 2.6 mg/Nm<sup>3</sup>.
- Line F is a dual pressure plant (N/M process) and has a capacity of 180 000 t/a. Working pressures are -0,08 bar (slight negative pressure) for ammonia oxidation and 3,8 bar for the absorption (pressures above atmospheric). As part of an adaptation project (1992), an SCR reactor has been installed in line F. The NO<sub>x</sub> concentration of the waste gas before the SCR reactor is 2,000–3,000 ppm (4,000–6,000 mg NO<sub>x</sub>/Nm<sup>3</sup> as NO<sub>2</sub>). The NO<sub>x</sub> concentration of waste gas leaving the SCR reactor is about 320–330 mg/Nm<sup>3</sup>. Ammonia slip is between 0.05 mg/Nm<sup>3</sup> and 0.10 mg/Nm<sup>3</sup>.

**Estimates of the main costs for the SCR process** are presented for retrofitting an SCR installation at an existing M/H plant and for an SCR installation in the course of adapting an old normal pressure plant (by construction of a new medium pressure absorption column). Data are based on information provided by [AGROLINZ 2000], with the exception of specific costs for electric energy and the specific costs for liquid ammonia. These costs were calculated by the Federal Environmental Agency Austria on basis of previous studies [cf. EGGER & WINTER, 2000; WIESENBERGER & KIRCHER 2001].

Table 8 presents main costs for **retrofitting an SCR reactor at an existing nitric acid plant** (M/H dual pressure plant). A waste gas volume of 110,000 Nm<sup>3</sup>/h, an NO<sub>x</sub> reduction of 0.3 g NO<sub>x</sub>/Nm<sup>3</sup> (as NO<sub>2</sub>) and a clean gas concentration of 200 mg NO<sub>x</sub>/Nm<sup>3</sup> (as NO<sub>2</sub>) are assumed. Production of nitric acid is assumed with 900 t/d.

Investment costs for the SCR installation are estimated at about 925,000 €, not including catalyst costs. Assuming a depreciation period of 15 years and an interest rate of 6 %, annual repayment on investment is about 95,400 €. Costs for maintenance and wear of 2 % of the entire investment costs are assumed; therefore, maintenance costs are estimated at about 18,500 €.

Main operating costs are annual catalyst costs and expenditures arising from consumption of energy and resources. Expenditures arising from heat displacement cannot be added to the SCR process, as heat displacement is required for an adiabatic operation of the waste gas expansion turbine. Function of staff referring to the operation of the SCR reactor is limited to routine inspection during operation. Personal expenses are neglected. Additional staff is usually not employed for the operation of an SCR installation.

For an SCR catalyst required for a reduction rate of 60–80 %, specific catalyst costs are about 18 €/kg. About 3,400 kg SCR catalyst are required for the NO<sub>x</sub> reduction described above. Assuming a lifetime of the SCR catalysts of 10 years and assuming an interest rate of 6 %, annual repayment on the SCR catalyst can be estimated at about 8,300 €/a.

Extra energy costs for the operation of the SCR reactor are caused by a power loss of the expansion turbine due to the pressure drop of the SCR reactor. This energy loss can be estimated on the basis of the pressure drop of the SCR reactor and the working pressure and working temperature before the waste gas expansion turbine. Operating conditions before the waste gas turbine are equated to the operating conditions of the SCR reactor. A power loss of the waste gas expansion turbine of about 8 kWh/h is estimated. Here, a working pressure of the SCR of 9 bar, a working temperature of 180 °C, a pressure drop of the SCR reactor of 10 mbar, and an efficiency of the waste gas expansion turbine of 70 % are assumed. The energy consumption of additional energy consumers is assumed with 10 kWh/h. Specific electric energy costs of 0.044 €/kWh were calculated by the Federal Environmental Agency Austria [cf. WIESENBERGER & KIRCHER, 2001]. Total extra energy costs for the SCR installation are calculated at about 6,710 €/a.

Resource costs arise from consumption of liquid ammonia which is provided as reducing agent. A stoichiometric molar rate of NO and NO<sub>2</sub> is to be expected in the waste gas of a nitric acid plant. According to reaction (I) and reaction (II) presented above, a stoichiometric consumption of ammonia results for the reduction of NO, whereas a molar rate of 2 results for the consumption of NH<sub>3</sub> at the reduction of NO<sub>2</sub>. Considering an NO<sub>x</sub> reduction of 0.3 g/Nm<sup>3</sup> (as NO<sub>2</sub>), ammonia consumption level is about 20 kg/h. Specific ammonia costs of 220 €/t were calculated by the Federal Environmental Agency Austria [cf. ECKER & WINTER, 2000]. Annual costs for liquid ammonia are about 35,500 €.

Operating expenses for reheating of the waste gas upstream the SCR reactor cannot be added to the SCR process, as heat displacement is integrated in the process for nitric acid production and required for an adiabatic operation of the waste gas expansion turbine. Reheating takes place by heat displacement of waste heat arising at catalytic ammonia oxidation. Finally, waste heat is recovered in a waste gas turbine downstream the SCR reactor.

Annual main costs for the SCR installation are estimated at about 185,300 €/a. With regard to the production of nitric acid, specific costs for the SCR installation are estimated at about 0.55 €/t HNO<sub>3</sub> (100 %). Specific extra costs for the abatement of NO<sub>x</sub> are 593 €/t NO<sub>x</sub>.

Table 8: Main costs for retrofitting an SCR reactor at an existing nitric acid plant (M/H dual pressure plant); a production of 900 t HNO<sub>3</sub>/d, a waste gas volume of 110,000 Nm<sup>3</sup>/h, an NO<sub>x</sub> reduction of 0.3 g NO<sub>x</sub>/Nm<sup>3</sup> (indicated as NO<sub>2</sub>) and a clean gas concentration of less than 200 mg NO<sub>x</sub>/Nm<sup>3</sup> (indicated as NO<sub>2</sub>) are assumed.

		€/unit	€/a
<b>operating parameter:</b>			
waste gas volume [Nm <sup>3</sup> /h]	110,000		
operating time [h/a]	8,400		
NO <sub>x</sub> concentration in crude gas [mg/Nm <sup>3</sup> as NO <sub>2</sub> ]	500		
NO <sub>x</sub> concentration in clean gas [mg/Nm <sup>3</sup> as NO <sub>2</sub> ]	200		
<b>investment costs excl. catalyst [€]</b>	<b>925,000</b>		
<b>repayment on investment incl. interest</b>			<b>95,400</b>
period of depreciation [a]	15		
interest rate [%]	6		
<b>maintenance and wear:</b>			<b>18,500</b>
maintenance and wear [% of investment costs]	2		
<b>energy consumption:</b>			
working pressure [bar]	9		
pressure drop of SCR reactor [mbar]	10		
working temperature of SCR reactor [°C]	190		
<b>extra energy consumption of compressor due to SCR reactor [kWh/h]<sup>1)</sup></b>	8	0.044 €/kWh <sup>1)</sup>	<b>3,050<sup>1)</sup></b>
<b>additional energy consumers [kWh/h]<sup>1)</sup></b>	10	0.044 €/kWh <sup>1)</sup>	<b>3,660<sup>1)</sup></b>
<b>SCR catalyst incl. interest (interest rate: 6 %)</b>			<b>8,300</b>
specific catalyst costs [€/kg]		18 €/kg	
amount of catalyst [kg]	3,400		
lifetime of catalyst [a]	10		
<b>liquid ammonia<sup>2)</sup></b>			<b>35,500<sup>2)</sup></b>
ammonia consumption [kg/h]:	20		
specific costs of liquid ammonia <sup>2)</sup>		220 €/t <sup>2)</sup>	
<b>ESTIMATED ANNUAL COSTS FOR SCR [€/a]</b>			<b>164,400<sup>2)</sup></b>
<b>SPECIFIC EXTRA COSTS REFERRING TO PRODUCED HNO<sub>3</sub> [€/t HNO<sub>3</sub>]</b>			<b>0.55<sup>2)</sup></b>
<b>SPECIFIC EXTRA COSTS FOR NO<sub>x</sub> ABATEMENT [€/t NO<sub>x</sub>]</b>			<b>593<sup>2)</sup></b>

<sup>1)</sup> Specific costs for electric energy of 0.044 €/kWh were calculated by the Federal Environment Agency Austria on basis of previous studies (cf. WIESENBERGER & KIRCHER, 2001).

<sup>2)</sup> Specific costs for liquid ammonia of 220 €/t were calculated by the Federal Environment Agency Austria on basis of previous studies (cf. ECKER & WINTER, 2000). In literature specific costs of ammonia for the emission control in nitric acid plants are indicated in the range between 100 \$/t (SCHWEFER et al., 2000) and 200 €/t (POTTIER, 2001). Different costs might be due to the fact, that ammonia is available on-site at a nitric acid plant. Calculating lower ammonia costs in the table above will decrease annual costs and specific extra costs for the SCR installation by about 15 %.

Table 9 presents estimates of main cost of an **SCR installation in the course of adapting an old normal pressure plant** (by construction of a new medium pressure absorption column). A waste gas volume of 65,000 Nm<sup>3</sup>/h, an NO<sub>x</sub> reduction of 4.0 g/Nm<sup>3</sup> (as NO<sub>2</sub>) and a production of 500 t/d are assumed. An NO<sub>x</sub> reduction rate of 92–95 % results with an assumed NO<sub>x</sub> input level between 4,000 and 6,000 mg/Nm<sup>3</sup> (as NO<sub>2</sub>) and an assumed NO<sub>x</sub> clean gas concentration of 320 mg/Nm<sup>3</sup> (as NO<sub>2</sub>).

Investment costs for an SCR installation are estimated at about 353,200 €, not including the catalyst costs. Assuming a depreciation period of 15 years and an interest rate of 6 %, annual repayment on investment is estimated at about 36,400 €. Costs for maintenance and wear are assumed with 2 % of the entire investment costs; maintenance costs are thus about 7,060 €.

Main operating costs are annual catalyst costs and expenditures arising from consumption of energy and resources. Function of staff referring to the operation of the SCR process is limited to routine inspection during operation. As above, personal expenditures are neglected. Also, expenditures arising from heat displacement are not added to the SCR process.

For an SCR catalyst required for a reduction rate of 95 %, specific catalyst costs are about 33 €/kg. The SCR catalyst weighs about 2,500 kg. Assuming a lifetime of the SCR catalysts of 10 years and an interest rate of 6 %, annual repayment on the SCR catalyst is estimated at about 11,300 €/a.

Extra energy costs for the use of the SCR reactor are caused by a power loss of the expansion turbine due to the additional pressure drop of the SCR reactor. The power loss of the expansion turbine is estimated at about 54 kWh/h. Here, a working pressure of the SCR reactor of 4.8 bar, a pressure drop of the SCR reactor of 50 mbar, a working temperature of the SCR reactor of 270 °C and an efficiency of the waste gas expansion turbine of 70 % are assumed. Energy consumption of additional energy consumers is assumed with 10 kWh/h. Specific electric energy costs of 0.044 €/kWh were calculated by the Federal Environmental Agency Austria [cf. WIESENBERGER & KIRCHER, 2001]. Total extra energy costs for the SCR installation are calculated at about 23,490 €/a.

Resource costs are caused by the consumption of liquid ammonia provided as reducing agent. A stoichiometric rate of NO and NO<sub>2</sub> is considered in the waste gas of nitric acid plants. According to reaction (I) and reaction (II) presented above, a stoichiometric consumption of ammonia results for the reduction of NO, whereas a molar rate of 2 results for the ammonia consumption at the reduction of NO<sub>2</sub>. Assuming a NO<sub>x</sub> reduction of 4.0 g/Nm<sup>3</sup> (as NO<sub>2</sub>), consumption of ammonia is about 144 kg/h. Specific costs for liquid ammonia of 220 €/t were calculated by the Federal Environmental Agency Austria [cf. ECKER & WINTER, 2000]. Annual costs for liquid ammonia are about 262,500 €.

Annual main costs for the SCR installation are estimated at about 340,900 €/a. With regard to the production of nitric acid, specific costs for the SCR installation are calculated at about 1.89 €/t HNO<sub>3</sub> (100 %).

Table 9: Main costs of an SCR installation in the course of adaptation of an old normal pressure plant (by construction of a new medium pressure absorption column); a production of 500 t/d, a waste gas volume of 65,000 Nm<sup>3</sup>/h, a crude gas concentration of 4,000 to 6,000 mg NO<sub>x</sub>/Nm<sup>3</sup> (as NO<sub>2</sub>) and a clean gas concentration of less than 350 mg NO<sub>x</sub>/Nm<sup>3</sup> (as NO<sub>2</sub>) are assumed.

		€/unit	€/a
<b>operating parameter:</b>			
waste gas volume [Nm <sup>3</sup> /h]	65,000		
operating time [h/a]	8,400		
NO <sub>x</sub> concentration in crude gas [mg/Nm <sup>3</sup> as NO <sub>2</sub> ]	4,300		
NO <sub>x</sub> concentration in clean gas [mg/Nm <sup>3</sup> as NO <sub>2</sub> ]	320		
<b>investment costs excl. catalyst [€]</b>	<b>353,200</b>		
<b>repayment on investment incl. interest</b>			<b>36,400</b>
period of depreciation	15		
interest rate [%]	6		
<b>maintenance and wear:</b>			<b>7,060</b>
maintenance and wear [% of investment costs]	2		
<b>energy consumption:</b>			
working pressure (bar)	4.8		
pressure drop of SCR reactor (mbar)	50		
working temperature of SCR reactor (°C)	270		
<b>extra energy consumption of compressor, due to SCR reactor [kWh/h]<sup>1)</sup></b>	54	0.044 €/kWh <sup>1)</sup>	<b>19,830<sup>1)</sup></b>
<b>additional energy consumers [kWh/h]<sup>1)</sup></b>	10	0.044 €/kWh <sup>1)</sup>	<b>3,660<sup>1)</sup></b>
<b>SCR catalyst incl. interest (interest rate: 6 %)</b>			<b>11,300</b>
specific catalyst costs [€/kg]		33 €/kg	
amount of catalyst [kg]	2,500		
lifetime of catalyst [a]	10		
<b>liquid ammonia</b>			<b>262,650<sup>2)</sup></b>
specific costs of liquid ammonia [€/t] <sup>2)</sup>		220 €/t <sup>2)</sup>	
ammonia consumption [kg/h]:	144		
<b>ESTIMATED ANNUAL COSTS FOR SCR [€/a]</b>			<b>340,900<sup>2)</sup></b>
<b>SPECIFIC EXTRA COSTS REFERRING TO PRODUCED HNO<sub>3</sub> [€/t HNO<sub>3</sub>]</b>			<b>1.89<sup>2)</sup></b>
<b>SPECIFIC EXTRA COSTS FOR NO<sub>x</sub> ABATEMENT [€/t NO<sub>x</sub>]</b>			<b>157<sup>2)</sup></b>

<sup>1)</sup> Specific costs for electric energy of 0.044 €/kWh were calculated by the Federal Environment Agency Austria on basis of previous studies (cf. WIESENBERGER & KIRCHER, 2001).

<sup>2)</sup> Specific costs for liquid ammonia of 220 €/t were calculated by the Federal Environment Agency Austria on basis of previous studies (cf. ECKER & WINTER, 2000). In literature specific costs of ammonia for the emission control in nitric acid plants are indicated in the range between 100 \$/t (SCHWEFER et al., 2000) and 200 €/t (POTTIER, 2001). Different costs might be due to the fact, that ammonia is available on-site at a nitric acid plant. Calculating lower ammonia costs in the table above will decrease annual costs and specific extra costs for the SCR installation by about 40 %.

In particular at plants with lower absorption pressure (and higher ammonia consumption levels for the abatement of  $\text{NO}_x$ ) operating costs strongly depend on specific ammonia costs. In literature specific costs of ammonia for emission control in nitric acid plants are indicated in the range between 100 \$/t [SCHWEFER et al., 2000] and 200 €/t [POTTIER, 2001]. Differences of ammonia costs might be due to the fact, that ammonia is available on-site at a nitric acid plant. Considering lower ammonia costs in the cost estimations above (Tables 3.4 and 3.5) will lower the annual costs and the specific extra costs by about 15–40 %, depending on the ammonia consumption level for the abatement of  $\text{NO}_x$ .

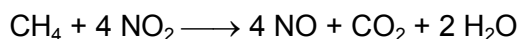
According to data provided by [CHEMCONNECT 2000], the price of nitric acid (68 %  $\text{HNO}_3$ ) is in the region of about 250–300 €/t.

### 3.4.1.2 Non-Selective Catalytic Reduction (NSCR)

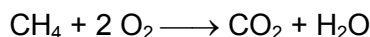
Non-selective catalytic reduction was widely used in nitric acid plants in the seventies. Due to high fuel expenses and high secondary emissions, the use of NSCR declined [EPA 1991] and is nowadays not favoured for new plants [GRY 1994].

At non-selective catalytic reduction processes (NSCR), fuel reacts with oxygen bound in  $\text{NO}_x$  on a catalyst. Hydrogen (of a preceding ammonia plant) or natural gas is used as fuel.

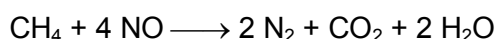
First  $\text{NO}_2$  is reduced to NO. The reduction of  $\text{NO}_2$  to NO results in a discoloration of waste gas:



Discoloration of the waste gas does not result in any reduction of  $\text{NO}_x$ . The fuel has to react completely with free oxygen present in the waste gas



before a complete reduction of  $\text{NO}_x$  from the waste gas occurs.



Preheating of the waste gas is necessary, as the reduction of  $\text{NO}_x$  takes place above a definite off-light temperature of the fuel. Using natural gas, waste gas has to be preheated up to 450–500 °C. With hydrogen, the preheating temperature is about 250–300 °C [THIEMANN et al. 1991, EPA 1991].

Reactions take place on a catalyst. Catalysts are made of palladium or mixtures of platinum and rhodium supported on alumina pellets or ceramic honeycomb substrate. Waste gas temperatures rise about 130°C (with use of natural gas) or 150°C (with use of hydrogen) for each percent of oxygen consumed. The working temperatures of catalysts are limited with about 840°C, this corresponds to a maximum  $\text{O}_2$  content of 2.8%. Heat from the catalytic reduction section is recovered in the waste gas expansion turbine. Expansion turbines have maximum working temperatures of about 650 °C, due to temperature limitation of the construction material. In order to meet temperature limitations of catalyst and waste gas absorption turbine, cooling of the waste gas with heat exchanger or two stage reduction systems with interstage heat recovery or with split streams are applied [EPA 1991].

**Characteristic features** of the NSCR technique for a complete reduction of NO<sub>x</sub> are:

- NO<sub>x</sub> reduction efficiencies in the range of 94–99 % are reported [EPA 1991]. High reduction rates are opposed to high secondary emissions and high fuel consumption.
- The reduction process is to a large extent influenced by free oxygen in the waste gas. The oxygen content of the waste gas leaving the absorption column is decisive for fuel consumption and for working temperature. The reduction of NO<sub>x</sub> requires high fuel consumption levels, as free oxygen in the waste gas has to be reduced. According to [BLANCO 1998] free oxygen content of waste gas is about 1–4 % at nitric acid plants. According to [DITTMAR 1985], an NSCR process at a nitric acid plant with a production of 120 t HNO<sub>3</sub>/d has a natural gas consumption of 1,000–1,300 Nm<sup>3</sup>/h.
- High secondary emissions of CO, CO<sub>2</sub>, HCN and VOC are caused by NSCR processes. VOC emissions of 700 to 3,000 mg/Nm<sup>3</sup> can be released. Total emissions of CO and VOC can amount to 4,000 ppm [DITTMAR 1985].
- Due to high working temperatures, the lifetime of catalysts is limited.
- N<sub>2</sub>O is reduced to N<sub>2</sub> and H<sub>2</sub>O
- For an oxygen content above 2.8 %, multistage NSCR processes have to be used, which meet the temperature limitations of the catalyst and the waste gas expansion turbine.

By application of NSCR techniques at nitric acid plants, cross media effects occur, such as high secondary emissions of CO, HCN, CO<sub>2</sub> and VOC and high levels of fuel consumption. For this reason, the **NSCR process cannot be considered state-of-the-art technology** for the reduction of NO<sub>x</sub> emissions.

### 3.4.2 End-of-pipe Processes Not or No Longer Applied for NO<sub>x</sub> Emission Reduction in Nitric Acid Plants

#### 3.4.2.1 Selective Non-catalytic Abatement Techniques (SNCR)

SNCR processes installed for example at power plants and cement plants are not suitable for a reduction of NO<sub>x</sub> emissions in nitric acid plants. SNCR techniques require working temperatures between 800 and 1,000 °C. Reheating of the waste gases up to these temperatures would be necessary. Waste gas temperatures of 800–1,000 °C are not achievable with heat displacement of the ammonia oxidation process alone. Reheating of the waste gases would cause high additional energy expenditures. Also, working temperatures between 800 and 1,000 °C exceed the maximum operation temperature of the waste gas expansion turbine.

#### 3.4.2.2 Adsorption Processes

Adsorption techniques for NO<sub>x</sub> abatement at nitric acid plants are mentioned in literature, such as the Pura-Siv-N process, the adsorption of NO<sub>x</sub> on molecular sieves and the pressure swing adsorption process [VDI 1982; THIEMANN et al. 1991; SCHMIDT and RICHTER 1986]. These processes are based on the adsorption of NO<sub>x</sub> at an adequate adsorbent and desorption of NO<sub>x</sub> at different temperature or pressure levels. These processes require high equipment and energy expenses and have not exceeded the experimental stage.

#### 3.4.2.3 Alkaline Final Absorption

At nitric acid plants, alkaline final absorption processes have been used for waste gas treatment before the installation of the SCR process. Waste gases were washed with sodium or magnesia hydroxide (or carbonate) or with solutions of ammonia. Other scrubbing techniques with H<sub>2</sub>O<sub>2</sub> or urea are described in literature [THIEMANN et al. 1991]. Their application at technical scale is not mentioned.



By the treatment of waste gases containing  $\text{NO}_x$  with alkaline solutions,  $\text{NO}$  and  $\text{NO}_2$  are absorbed at equal volume portions under formation of nitrites. By application of ammonia scrubbing, the formation of ammonium nitrite is suppressed by aeration and ammonium nitrate is formed in a three-stage process [THIEMANN et al. 1991]. In Austria, alkaline final absorption processes were in operation for  $\text{NO}_x$  abatement at nitric acid plants before installation of SCR. Alkaline final absorption processes are not suitable for achieving low  $\text{NO}_x$  emission levels, as only limited reduction could be reached [EFMA 1995], [VDI 1983]. Cross media effects occur, such as the development of considerable amounts of scrubbing solution. Alkaline final absorption cannot be considered state-of-the-art technology.

### 3.4.3 Process Integrated Measures for the Reduction of $\text{NO}_x$ Emissions – Measures for Achieving High Absorption Efficiencies

High absorption efficiencies are relevant in order to minimise ammonia consumption level and to minimise  $\text{NO}_x$  concentration in the waste gas leaving the absorption column. High absorption efficiencies mainly result from high pressures applied to the absorption step. In order to achieve high absorption efficiencies, the design of absorption columns and low absorption temperature are also relevant.

With the exception of application of high absorption pressures, measures related to the absorption process result only in a limited reduction of  $\text{NO}_x$  and are taken in addition to further measures for the reduction of  $\text{NO}_x$  emissions.

#### 3.4.3.1 Absorption Pressure

Absorption pressure is a decisive factor for the  $\text{NO}_x$  concentration of the waste gas leaving the absorption column. The oxidation of  $\text{NO}$  into  $\text{NO}_2$  and the absorption of  $\text{NO}_2$  in water strongly depend on absorption pressure. Higher pressures result in higher absorption efficiencies and lower  $\text{NO}_x$  emission levels.

With absorption pressures of 15 bar applied at an M/H pressure plant (5/15 bar),  $\text{NO}_x$  emission levels of 100–300  $\text{mg}/\text{Nm}^3$  are achievable depending on the concentration of the nitric acid produced and on economic considerations [INFOMIL, 1999].

Absorption pressures of nitric acid plants are at least above 3–4 bar. Plants with absorption columns operating at lower pressures (e.g. absorption at atmospheric pressure) do not correspond to state-of-the-art technology. These processes show rather low efficiencies with regard to ammonia input and are characterised by very high  $\text{NO}_x$  concentrations downstream the absorption column (> 6,000 ppm).

Improvement of absorption efficiency by increasing the absorption pressure is not applicable to existing absorption columns, as the absorption column of a nitric acid plant usually is designed for a definite pressure. Achieving higher absorption efficiency by providing a higher absorption pressure is only possible if the absorption column is rebuilt and designed for adequate pressures.

**Reference plant:** As part of an adaptation project of an old nitric acid plant working at atmospheric pressure, a new absorption section was built at the Agrolinz Melamin GmbH in 1994 (Line F). The old normal pressure absorption column was replaced by a new absorption column working at 3.8 bar (pressure above atmospheric). Additionally, an SCR process was installed to reduce  $\text{NO}_x$  emissions.

### 3.4.3.2 Absorption Temperature

As low temperatures favour the oxidation of NO and the absorption of NO<sub>2</sub>, efficient cooling systems are important in order to reach high efficiencies. Absorption columns equipped with sieve plates are cooled with inside water-cooled cooling coils. Waste heat, which arises in particular from the formation of acid at the lower region of the absorption column has to be carried off in order to obtain high absorption yields.

Absorption columns with efficient cooling systems are operated at temperatures of 20–30 °C. Applying lower temperatures, e.g. by cooling with chilled water, further decreases the NO<sub>x</sub> emission level. Additional cooling with refrigeration cooling systems is applied e.g. in extended absorption systems for increasing absorption efficiencies and for further reduction of NO<sub>x</sub> emissions. Therefore, the lower portion of the column is cooled by normal cooling water available at the plant site. Chilled water or coolant provided by closed-loop refrigeration system cools the remaining trays to approximately 2° to 7°C. For additional cooling, cold arising by the ammonia vaporisation system could be used. Cooling devices are related to higher expenses for equipment and energy and are particularly applied in addition to other emission reduction measures, as extended absorption [EPA 1991, THIEMANN et al. 1991].

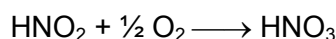
### 3.4.3.3 Absorption Column Design

In addition to absorption pressure and absorption temperature, high absorption efficiency is dependent on the design of the absorption column. Essential parameters of absorption column design are volume of the absorption column, number and structure of sieve trays, and distance between sieve trays. At equal pressure levels, absorption efficiency increases with the volume of the absorption column and with the number of sieve trays. Cross media effects do not take place, as NO<sub>x</sub> is converted to additional HNO<sub>3</sub>. However, even large additional absorption volumes only result in small reduction of NO<sub>x</sub> emissions, as the oxidation of nitrogen monoxide into nitrogen dioxide proceeds rather slowly when the NO<sub>x</sub> concentration is low [THIEMANN et al. 1991].

- **Extended absorption:** The number of sieve trays is increased by the installation of an additional absorption column. NO<sub>x</sub> emissions are reduced due to a better absorption efficiency. An additional absorption column consists only of few sieve trays, as spacing between the sieve plates increases with falling NO<sub>x</sub> concentration. The additional absorption volume has to be constructed with stainless steel and causes rather high expenses. Further NO<sub>x</sub> abatement can be achieved by additional cooling systems [OHSOL 1990, EPA 1991 and THIEMANN et al. 1991]. According to [GRY 1994] extended absorption with water is suitable for reduction of NO<sub>x</sub> emissions at existing nitric acid plants with an absorption pressure of at least 8 to 10 bar.

Extended absorption with water has been used especially in the United States. For applying absorption pressures of about 9 bar and additional cooling, and NO<sub>x</sub> emissions of 0.65 to 1.4 kg NO<sub>x</sub>/t HNO<sub>3</sub>, corresponding to about 200 to 500 mg NO<sub>x</sub>/Nm<sup>3</sup> (as NO<sub>2</sub>) and reduction rates of 93–97 % are reported [EPA 1991]. According to [GRY, 1994] NO<sub>x</sub> emissions of 200 and 600 ppm, corresponding to 410–1230 mg NO<sub>x</sub>/Nm<sup>3</sup> (as NO<sub>2</sub>) are achieved with absorption pressures above 8 bar. Here, NO<sub>x</sub> reduction rates of > 74 % can be estimated.

- **Highly efficient absorption (HEA):** While conventional absorption is based on the partial oxidation of the HNO<sub>2</sub> intermediate which evolves nitrogen monoxide (NO) gas, high efficiency absorption technology is based on the enhanced oxidation of the nitrous acid (HNO<sub>2</sub>) intermediate in the liquid phase [ENVIRO-CHEM, 2000]. According to [BOTTON and COSSERAT, 1983] a better absorption efficiency could be reached if the transformation of HNO<sub>2</sub> (assumed as the soluble form of NO<sub>x</sub>) into HNO<sub>3</sub> is considered as the reaction that limits the total rate of flow of converted gas. As a consequence, the absorption column design is modified in order to promote the conversion of the HNO<sub>2</sub> into HNO<sub>3</sub> in the liquid phase.



The absorption column is modified by increasing the height of the liquid emulsion, particularly at the last downstream plates of the installation [BOTTON & COSSERAT, 1983]. According to [ENVIRO-CHEM, 2000] highly efficient absorption (HEA) processes are suited for combination with selective catalytic reduction. The HEA column converts the majority of  $\text{NO}_x$  into  $\text{HNO}_3$  and the SCR process (cf. chapter 3.4.1) removes the remaining  $\text{NO}_x$ . Recovery of nitric acid and lower consumption of ammonia is possible. Processes with a combined HEA and SCR process are reported to achieve a reduction from 3,500 ppm to 700 ppm  $\text{NO}_x$  with high efficient absorption. Further reduction of  $\text{NO}_x$  is obtained by selective catalytic abatement [ENVIRO-CHEM, 2000].

### 3.5 Reduction of $\text{N}_2\text{O}$ Emissions

With regard to the relevance of  $\text{N}_2\text{O}$  as a contributor to global warming several projects are run by industry and research institutes for developing  $\text{N}_2\text{O}$  abatement processes. First promising results have been reported on catalytic  $\text{N}_2\text{O}$  abatement processes, which are referred to in chapter 3.5.3. Some of these promising techniques might be available in the near future. A commercialised and patented process for the decomposition of  $\text{N}_2\text{O}$  in the  $\text{NH}_3$  combustion unit (homogenous decomposition) is available for new nitric acid plants (cf. chapter 3.5.2).

Generally, a high efficiency of the catalytic ammonia oxidation is important to reduce  $\text{N}_2\text{O}$  formation. The efficiency of the ammonia conversion is dependent on operating conditions such as pressure level, gas velocity and reaction temperature and on the catalyst (cf. chapter 3.5.1).

According to their position within the nitric acid plant processes for the abatement of  $\text{N}_2\text{O}$  emissions, the relevant measures can be classified into three categories:

- measures for the reduction of  $\text{N}_2\text{O}$  formation – primary measures
- processes for the decomposition of  $\text{N}_2\text{O}$  in the  $\text{NH}_3$  combustion unit – secondary measures
- processes for the decomposition/reduction of  $\text{N}_2\text{O}$  in the tail gas of a nitric acid plant (downstream the absorption unit) – tertiary measures.

Table 10 presents a summary of available and emerging techniques for the abatement of  $\text{N}_2\text{O}$  emissions from nitric acid plants. In the table the status (3/2001) of these techniques is indicated.

Table 10: Summary of available and emerging techniques for the N<sub>2</sub>O abatement from nitric acid plants including the current status (3/2001) of these techniques

	Characteristics	Current status (3/2001)	(Expected) N <sub>2</sub> O reduction	References
<b>Measures for the reduction of N<sub>2</sub>O formation – primary measures</b>				
<ul style="list-style-type: none"> <li>• Modifications of the gauze geometry and density of Pt/Rh catalysts</li> </ul>	<ul style="list-style-type: none"> <li>- increase in NO yield</li> <li>- limited N<sub>2</sub>O reduction</li> </ul>	catalysts with knitted gauzes are provided by catalyst manufacturer	?	Schwefer et al. (2000)
<ul style="list-style-type: none"> <li>• CO<sub>3</sub>O<sub>4</sub> catalyst for the NH<sub>3</sub> combustion</li> </ul>	<ul style="list-style-type: none"> <li>- high NO losses</li> </ul>	?	~ 80 %	Schwefer et al. (2000)
<b>Processes for the decomposition of N<sub>2</sub>O in the NH<sub>3</sub>-combustion unit – secondary measures</b>				
<ul style="list-style-type: none"> <li>• Homogenous decomposition</li> </ul>	<ul style="list-style-type: none"> <li>- high investment costs</li> <li>- no operating costs</li> <li>- difficult (expensive) revamp of existing plants</li> <li>- not applicable on low pressure combustion units</li> </ul>	patented process; commercially available	70–85 %	Schöffel et al. (2001); Kongshaug (1998).
<ul style="list-style-type: none"> <li>• Catalytic decomposition of N<sub>2</sub>O in the NH<sub>3</sub>-combustion unit</li> </ul>	<ul style="list-style-type: none"> <li>- cost effective</li> <li>- applicable to almost all (also existing) plants</li> <li>- potential product losses and contamination</li> </ul>	full scale trial at three plants since 3/1999, 7/1999 and 1/2000; full scale trial at one plant since 5/2000	~ 80 %	Kuhn (2001)
<b>Processes for the decomp./reduction of N<sub>2</sub>O in the tail gas (downstream the absorption unit) – tertiary measures</b>				
<ul style="list-style-type: none"> <li>• Non-selective catalytic reduction (NSCR)</li> </ul>	<ul style="list-style-type: none"> <li>- simultaneous reduction of NO<sub>x</sub> and N<sub>2</sub>O</li> <li>- high secondary emissions</li> <li>- high fuel consumption</li> </ul>	NO <sub>x</sub> abatement process installed at some older plants; NSCR cannot be considered state-of-the-art technology	~ 85 %	Schwefer et al. (2000) Dittmar (1985).
<ul style="list-style-type: none"> <li>• Catalytic decomposition</li> </ul>	<ul style="list-style-type: none"> <li>- only applicable at temperatures above 400 °C</li> </ul>	tests on laboratory scale (model tail gas) and tests at pilot plants (side stream of the waste gas of a nitric acid plant)	depending on temperature and catalyst	Schwefer et al. (2000) Maurer & Groves (2001); Mul et al. (2001), Kieger et al. (2001); van den Brink et al. (2000); van den Brink (2001)
<ul style="list-style-type: none"> <li>• Catalytic reduction</li> </ul>	<ul style="list-style-type: none"> <li>- requires reducing agent such as NH<sub>3</sub>, propane (LPG) or natural gas</li> </ul>			

### 3.5.1 Measures for the Reduction of N<sub>2</sub>O Formation – Primary Measures

#### 3.5.1.1 Operating Conditions

The efficiency of ammonia conversion declines with higher pressures. However, as the pressure level of the ammonia combustion unit is defined with the design of the nitric acid plant, a modification of the pressure of an existing combustion unit is not possible.

For economic reasons, new plants are equipped with medium or high pressure ammonia conversion units. Compared to lower pressure levels, gas volumes are smaller and equipment can be built at lower expense. The N<sub>2</sub>O emissions from nitric acid production have increased slightly over the last 30 years, due to the application of higher pressure levels with catalytic ammonia conversion [KONGSHAUG, 1998].

At specific pressure levels, optimum ammonia conversion is dependent on the combustion temperature (cf. chapter 3.2). As the reaction temperature is related to the ammonia/air ratio (an increase in the proportion of ammonia of 1 % increases the temperature by ca. 68 K), the ammonia/air ratio has to be controlled accurately to achieve an optimum conversion rate [THIEMANN et al. 1991].

#### 3.5.1.2 Catalysts

In order to achieve high ammonia conversion efficiencies, catalysts with knitted gauzes have been developed in the early 1990s and are now provided by all major catalyst manufacturers [SCHWEFER et al., 2000].

A good condition of the catalyst is important for a high ammonia oxidation rate. Accurate filtering of air and ammonia input is important to prevent poisoning of the catalyst. Due to precious metal loss, catalyst activity gradually decreases. Catalysts are exchanged at a loss of about 20 to 40 %.

### 3.5.2 Available Measures for the Reduction of N<sub>2</sub>O Emissions

#### 3.5.2.1 Non-selective Catalytic Reduction (NSCR)

By using NSCR, a simultaneous reduction of NO<sub>x</sub> and N<sub>2</sub>O is possible. However, this process results in high secondary emission levels and high fuel consumption levels, therefore the NSCR process cannot be considered state-of-the-art technology (cf. chapter 3.4.1).

#### 3.5.2.2 Homogenous Decomposition in the Ammonia Combustion Unit

A commercialised and patented abatement process based on the thermal decomposition of N<sub>2</sub>O in the hot zone down-stream the ammonia combustion gauzes is reported to be most suitable for new plants. N<sub>2</sub>O is unstable with respect to its decomposition into nitrogen and oxygen at temperatures above 870 °C. As the decomposition reaction takes several seconds, an extra reaction volume is provided between the platinum catalyst gauze and the heat exchanger. Combustion gases have extra retention time before they are cooled and conducted to the absorption column. During this retention time, nitrous oxide (N<sub>2</sub>O) is decomposed into N<sub>2</sub> and O<sub>2</sub>. The reduction of N<sub>2</sub>O emissions depends on the dimension of the reactor and on the heat loss within the reactor and is up to about 85 %. The method is not suited for plants with ammonia oxidation at atmospheric pressure [FAREID et al., 1988; KONGSHAUG 1998; SCHÖFFEL, 2001].

**Reference plant:** An oxidation reactor based on an extended reaction chamber was successfully installed by Hydro Agri at a 2,000 t/d nitric acid plant in Porsgrunn, Norway. This process allows a reduction of N<sub>2</sub>O emissions of at least 70–85 %. A plant with modern technology would

therefore have an emission of 2.5 t CO<sub>2</sub> eq./t N corresponding to about 1.8 kg N<sub>2</sub>O/t HNO<sub>3</sub>. Specific abatement costs are reported to be in the order of 6–10 €/t CO<sub>2</sub>-equivalent [KONG-SHAUG 1998; SCHÖFFEL et al. 2001].

### 3.5.3 Emerging Techniques for the Reduction of N<sub>2</sub>O Emissions

Emerging techniques concerning emission control at nitric acid production mainly refer to the abatement of N<sub>2</sub>O emissions. Several projects are run by industry and research institutes for developing N<sub>2</sub>O abatement processes. First promising results of full technical scale tests on the catalytic decomposition of N<sub>2</sub>O in the ammonia combustion unit are already available.

#### 3.5.3.1 Modifications of the Catalyst for Ammonia Conversion

Apart from the development of Pt/Rh catalysts with knitted gauzes (cf. chapter 3.5.1) further improvements concerning the geometry and density of gauzes have been achieved recently [SCHWEFER et al., 2000].

Cobalt oxides were reported to generate less nitrous oxides than precious metal catalysts, but they also showed lower ammonia conversion efficiencies, high product losses and deactivation and inhibition phenomena [SCHWEFER et al., 2000].

#### 3.5.3.2 Catalytic Decomposition of N<sub>2</sub>O in the Ammonia Combustion Unit

N<sub>2</sub>O is unstable at temperatures which are found in the ammonia combustion unit, however the decomposition reaction into N<sub>2</sub> and O<sub>2</sub> takes several seconds. The main idea of this process is to enhance the decomposition rate with a catalyst installed directly downstream the noble metal catalyst. As no additional retention time and therefore no extra reaction volume would be required for the decomposition, the catalyst could be installed in a simple manner in almost all combustion units. This process would also be suitable for retrofitting into existing nitric acid plants. Catalysts for the catalytic N<sub>2</sub>O decomposition in the ammonia conversion unit are already being tested on a technical scale at the following installations:

In an atmospheric combustion plant at BASF Ludwigshafen, the N<sub>2</sub>O concentration of about 1,000 ppm downstream of the noble metal gauzes decreases to 100–200 ppm downstream of the catalyst bed. In two plants at BASF Antwerp, where the combustion process is operated at a pressure of 5.5 bar, the N<sub>2</sub>O concentration decreases from approx. 1200 ppm to 500 ppm and from about 1,400 ppm to 250 ppm. The trials at Ludwigshafen have been running since March 1999, at Antwerp since July 1999 and since January 2000 (status 03/2001). Expected catalyst costs (including the licensing fee) for a 500 mtpd HNO<sub>3</sub> (100%) plant with a combustion at medium pressure (5 bar) have been estimated at about 250,000 €/m<sup>3</sup>. The lifetime of the catalyst has been indicated with at least two years. Before BASF is prepared to make this process available to other nitric acid producers, further research work has to be done in order to confirm the performance and lifetime of the catalyst [KUHN, 2001].

At a medium nitric acid plant of NORSK HYDRO, a catalyst for the decomposition of N<sub>2</sub>O in the ammonia combustion unit was installed in March 2000, which exhibits conversion in excess of 90 % (status 03/2001) [SCHÖFFEL et al., 2001].

### 3.5.3.3 Catalytic Decomposition/Reduction of N<sub>2</sub>O in the Tail Gas

Several catalytic materials have been considered for the decomposition or reduction of N<sub>2</sub>O [KAPTEIJN, 1996]. Substituted zeolites of the type BETA, MOR, MFI, MEL and FER are promising candidates for the decomposition or reduction of N<sub>2</sub>O. Cu, Fe, Mn, Co, Ni, Pd, Ru, Rh are among the substituting cations. Other possible catalysts are calcined hydrotalcites, perovskites and some mixed metal oxides [SCHWEFER et al., 2000].

Processes for the reduction of N<sub>2</sub>O have been installed successfully at adipic acid plants<sup>7)</sup> and have already led to a significant reduction of N<sub>2</sub>O emissions. However, due to different waste gas conditions, N<sub>2</sub>O abatement techniques for adipic acid plants cannot be directly applied for the abatement of N<sub>2</sub>O from nitric acid plants. The main difficulties arise with the presence of water vapour, nitric oxides and oxygen in the waste gas of a nitric acid plant, which could inhibit or deactivate catalyst materials.

Several catalysts considered for the N<sub>2</sub>O abatement in nitric acid plants have already been studied under laboratory conditions with model tail gases [SCHWEFER et al. 2000; VAN DEN BRINK et al. 2000; VAN DEN BRINK, 2001; MAURER & GROVES, 2001; MUL et al., 2001; KIEGER et al., 2001]. Catalysts have been tested without reducing agents (catalytic decomposition of N<sub>2</sub>O) and in combination with reducing agents (selective catalytic reduction of N<sub>2</sub>O). Direct catalytic decomposition of N<sub>2</sub>O (without reducing agents) seems only feasible for plants with tail gas temperature levels of at least 400 °C. These temperatures are available in tail gases of nitric acid plants with high pressure absorption (approx. 1/3 of the European nitric acid plants). For plants with waste gas temperatures below 400 °C, selective catalytic reduction (SCR) of N<sub>2</sub>O is an alternative. This technique can in principle be used in any nitric acid plant, either upstream or downstream the expander. Removal of N<sub>2</sub>O by SCR requires the use of a reducing agent (natural gas or LPG). The reducing agent contributes considerably to the cost efficiency of N<sub>2</sub>O reduction by SCR [VAN DEN BRINK, 2000].

According to [MAURER & GROVES, 2001] long term tests for catalytic decomposition are currently in progress in a pilot plant by using the side stream of a nitric acid plant. Tests on pilot plant scale are also reported by [KIEGER et al., 2001]. As far as it is known no results have been published from full technical scale trials on the catalytic decomposition/reduction of N<sub>2</sub>O of the tail gas of a nitric acid plant (status 3/2001).

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<sup>7</sup> An N<sub>2</sub>O abatement process for an adipic acid plant has also been integrated successfully into the waste gas train of a nitric acid plant. Here, waste gas of an adipic acid plant containing NO<sub>2</sub> is piped into the nitric acid plant and HNO<sub>3</sub> is recovered from the adipic acid waste gas by absorption of NO<sub>2</sub> in water. The N<sub>2</sub>O decomposition unit is installed downstream the absorption column of the nitric acid plant. Technically it is better to carry out the N<sub>2</sub>O decomposition in the absence of large amounts of NO/NO<sub>2</sub>, and to utilise the pressure level of the existing nitric acid compressor [KUHN, 2001].

## 4 WASTEWATER

### 4.1 Process Condensates

At the production of weak nitric acid, wastewater do not arise from process condensate. Process condensates of the catalytic ammonia oxidation containing 2–3 % HNO<sub>3</sub> (low-pressure ammonia oxidation) to 40 % HNO<sub>3</sub> (high-pressure ammonia oxidation) are separated after cooling the nitrous gas stream and are completely used in the absorption section for the production of weak acid.

At the production of concentrated nitric acid by direct processes, more process condensates arise from the combustion process than can be reused by the process. Process condensates also arise from the production of concentrated nitric acid by indirect processes. Process condensates are used in other (fertiliser) production processes or are discharged after adequate wastewater treatment.

### 4.2 Periodic Blowdown

Ammonia input usually contains residual water and hydraulic oils. By evaporating ammonia, these substances remain in the evaporator and are drained by gravity to an ammonia stripper. The residual water contains high amounts of ammonia which is stripped with steam [THIEMANN et al. 1991, ENVIRO-CHEM 2000]. The remaining oil/water mixture is separated by a water/oil centrifugal [AGROLINZ 1999]. Waste oil requires adequate waste treatment.

In order to avoid formation of ammonium salts, water or steam is periodically sprayed into the suction of the nitrous gas compressor [THIEMANN et al. 1991]. Emissions from the purging and sampling points are collected and pumped back to the nitric acid plant [EFMA 1995].

### 4.3 Diffuse Emissions

Leaks from pumps, vessels, etc. are pumped into a separate acid drain tank and then processed directly or indirectly. The apparatus used for this purpose is totally separated from the sewage system in order to prevent contamination of wastewater [THIEMANN et al. 1991].

### 4.4 Cooling Water

Cooling water is required for cooling the nitrous gas stream to low temperatures, so that water formed during ammonia oxidation condenses. Reaction heat released in the absorption column has to be carried off by cooling water, so that absorption temperatures are about 20–30 °C. Table 11 presents consumption of cooling water at Austrian plants.

Table 11: Consumption of cooling water at Austrian plants

	Line E – M/H process	Line F – N/M process
Consumption of cooling water [m <sup>3</sup> /h] [m <sup>3</sup> /t HNO <sub>3</sub> ]	1,800–3,000 50–84	1,300–2,000 60–93
Temperature difference	≤ 10 °C	≤ 10 °C



## 5 WASTES AND RESIDUES

### 5.1 Filters

Typical filter media for filtering air are plastic or glass fibres. Filter media for filtering ammonia are Teflon or sintered metals. For filtering NH<sub>3</sub>/air-mixtures, ceramic filter cartridges are used. Air filters are replaced regularly, because filter materials can tear or become overload and cause excessive pressure drops. Filter life depends on the particulate load in the air [THIEMANN et al. 1991].

Used filter cartridges can be cleaned and reused or are disposed [EFMA 1995]. However, reusing filter material should not reduce the efficiency of the filtering installations.

### 5.2 Waste Oils

At nitric acid plants, waste oils arise due to periodical replacement of the lubricating oil in rotating machines, such as compressors, turbines and pumps [EFMA, 1996].

Contamination of ammonia with water and hydraulic oils (from ammonia plants) is removed in a two-step evaporator. The water/oil mixture arising with this procedure is separated in centrifuges [AGROLINZ, 1999].

Waste oils require adequate disposal.

### 5.3 Spent Catalysts

Due to catalyst losses, ammonia oxidation catalysts are periodically replaced. Recovery systems consisting of palladium gauzes are used for recovery of precious metals. Recovery systems are replaced periodically.

Ammonia oxidation catalysts and catalyst recovery gauzes are reprocessed by the catalyst manufacturer. The recovered precious metals are used for the production of new catalysts [EFMA 1995, MATTHEW JOHNSON 2000]. Precious metals which could not be recovered precipitate on cold installation parts or can be found in the acid tank. Precipitated precious metals are reprocessed [JOHNSON MATTHEW 2000].

Spent catalysts of the NO<sub>x</sub> abatement processes are discharged or returned to the catalyst manufacturer [EFMA 1995].

## 6 NITRIC ACID PLANTS IN AUSTRIA

In Austria, weak nitric acid (59.7 % HNO<sub>3</sub>) is produced in two plants (N/M process and M/H process) in one location. The entire capacity of HNO<sub>3</sub> production is about 480,000 t/a (based on 100 % HNO<sub>3</sub>). Nitric acid is mainly used for the production of fertilisers. About 95 % of the nitric acid is used as raw material producing NPK fertilisers and ammonium nitrate based fertilisers. The production of technical ammonium nitrate is also of relevance.

Table 12: Summary of the Austrian nitric acid plants [AGROLINZ, 1999, AGROLINZ 2000]

	Line E (M/H process)	Line F (N/M process)
<b>Input/output levels:</b>		
• Capacity (related to 100 % HNO <sub>3</sub> )	300,000 t/a	180,000 t/a
• NH <sub>3</sub> input 1997	87,360 t	51,500 t
• NH <sub>3</sub> input 1998	91,700 t	52,330 t
• HNO <sub>3</sub> production 1997 (related to 100 % HNO <sub>3</sub> )	307,660 t	181,570 t
• HNO <sub>3</sub> production 1998 (related to 100 % HNO <sub>3</sub> )	321,400 t	183,430 t
<b>Ammonia oxidation:</b>		
• Pressure for catalytic NH <sub>3</sub> oxidation (pressure above atmospheric)	3.3 bar	-0.08 bar
• Oxidation temperature	895 °C	840–850 °C
<b>Absorption:</b>		
• Pressure for absorption (pressure above atmospheric)	8 bar	3.8 bar
• Absorption temperature	25 °C	25 °C
<b>Air emissions:</b>		
• Waste gas volume	112,000 Nm <sup>3</sup> /h	65,500 Nm <sup>3</sup> /h
• NO <sub>x</sub> abatement process	SCR reactor	SCR reactor
NO <sub>x</sub> concentration after SCR reactor [ppm]	90 ppm	155–160 ppm
[mg NO <sub>x</sub> /Nm <sup>3</sup> ] <sup>1)</sup>	180–190 mg/Nm <sup>3</sup>	320–330 mg/Nm <sup>3</sup>
[kg NO <sub>x</sub> /t HNO <sub>3</sub> ] <sup>1) 2)</sup>	0.54–0.56 kg/t HNO <sub>3</sub>	0.98–0.99 kg/t HNO <sub>3</sub>
NH <sub>3</sub> slip [ppm]	0.34–3.4 ppm	0.07–0.13 ppm
[mg NH <sub>3</sub> /Nm <sup>3</sup> ]	0.26–2.6 mg/Nm <sup>3</sup>	0.05–0.10 mg/Nm <sup>3</sup>
N <sub>2</sub> O concentration in waste gas [ppm]	1,000–1,400 ppm	600–800 ppm
[mg/Nm <sup>3</sup> ]	1,960–2,750 mg/Nm <sup>3</sup>	1,180–1,570 mg/Nm <sup>3</sup>
[kg/t HNO <sub>3</sub> ] <sup>2)</sup>	5.8–8.1 kg/t HNO <sub>3</sub>	3.6–4.8 kg/t HNO <sub>3</sub>

<sup>1)</sup> as NO<sub>2</sub>

<sup>2)</sup> related to 100 % HNO<sub>3</sub>

## 7 LEGISLATIVE REGULATIONS

### 7.1 Austria

#### 7.1.1 Emissions to Air

In Austria, nitric acid plants are subjected to the “Gewerbeordnung” BGBl. 194/1994 idgF. (industry, trade and licensing regulations; Federal Legal Gazette 194/1994). According to the “Gewerbeordnung”, the competent authority has to limit emissions of atmospheric pollutants in accordance with what is considered state-of-the-art. An explicit regulation for nitric acid plants does not exist. Emission limits are set in the permit issued by the local authority. For authorisations to be granted for construction, modification and operation of a plant, the competent authority takes into account TA-Luft and VDI-guidelines as well as current developments of the industry. Table 5.1 presents current emission limits stipulated for the only production in Austria (Linz, Upper Austria). The Austrian nitric acid plants are officially inspected every 5 years. [FIERLINGER 1999].

Table 13: Current NO<sub>x</sub> emission limits for nitric acid production set in the permit issued by the local authority in 1994 [FIERLINGER 1999]

	half-hour average	daily average
NO <sub>x</sub> emission limit	55 kg NO <sub>x</sub> /h referred to NO <sup>1)</sup>	50 kg NO <sub>x</sub> /h referred to NO <sup>2)</sup>
	In case of exceeding the emission limits including start-up or shut-down operations, the stipulated daily average limit of 50 kg NO <sub>x</sub> /h has to be met within 24 hours after the incident. This period of time starts the moment the emission limit is exceeded.	

<sup>1)</sup> Taking into account the total waste gas volume of 177,500 Nm<sup>3</sup> released by the two nitric acid plants (cf. table 4.1) the emission limit corresponds to an NO<sub>x</sub> concentration of approximately 475 mg/Nm<sup>3</sup> referred to NO<sub>2</sub>.

<sup>2)</sup> Taking into account the total waste gas volume of 177,500 Nm<sup>3</sup> released by the two nitric acid plants (cf. table 4.1) the emission limit corresponds to an NO<sub>x</sub> concentration of approximately 430 mg/Nm<sup>3</sup> referred to NO<sub>2</sub>.

#### 7.1.2 General Licensing Requirements

As mentioned above, the application of BAT is mandatory for new plants. Stricter regulations may be imposed, if this is necessary to ensure compliance with EU ambient air quality limit values. In addition, the operation of the plant should not lead to an excess of (Austrian) ambient air quality limit values.

#### 7.1.3 Ambient Air Concentration

The Austrian Air Protection Act (Federal Gazette I 115/97 amended by Federal Gazette I 62/2001) establishes ambient air quality limit values for several pollutants for the protection of human health. The Austrian Air Quality Protection Act fully transposes the Air Quality Framework Directive (96/62/EC) and its first two daughter Directives (1999/30/EC and 2000/69/EC). Table 14 presents ambient air quality limit values that were fixed for NO<sub>2</sub>.

Table 14: Ambient air quality limits for NO<sub>2</sub>

Pollutant	concentration	averaging period	Margin of tolerance
NO <sub>2</sub>	200 µg/m <sup>3</sup>	30 min	–
NO <sub>2</sub>	30 µg/m <sup>3</sup>	annual	30 µg/m <sup>3</sup> on the entry into force (2001); reducing from 1.1.2002 and every 12 months thereafter by 5 µg/m <sup>3</sup> until 2005. A margin of tolerance of 10 µg/m <sup>3</sup> applies from 1.1. 2005 until 31.12.2009. A margin of tolerance of 5 µg/m <sup>3</sup> applies from 1.1. 2010 bis 31.12.2011. The limit value has to be met by 1.1.2012.

#### 7.1.4 Air Quality Management Plans

If the sum of the limit value and margin of tolerance was exceeded and this excess pollution was not caused by an accident, an air quality management plan has to be established. Such a plan might include specific measures for installations, such as

1. Application of Best Available Technology (BAT), according to the date of the enter into force of the action plan.
2. Use of fuels with low emissions
3. Establishment of specific plans for single plants
4. Enforcement of emission caps.

#### 7.1.5 Wastewater Regulations

The "**Abwasseremissionsverordnung anorganische Düngemittel**" (ministerial ordinance for the limitation of wastewater emissions of the production of inorganic fertilisers and phosphoric acid and its salts) among others applies for the production of nitrogen fertilisers (**nitric acid**, ammonium nitrate, calcium-ammonium-nitrate, ammonium sulphate and ammonium-sulphate-nitrate). The AEV Düngemittel does not apply to the discharge of wastewater from cooling systems, steam generators or water conditioning. Table 15 gives the parameters relevant for the discharge of wastewater at the production of nitrogen fertilisers.

In accordance with the AEV "anorganische Düngemittel" the following measures are taken to reduce emissions at installations for the production of nitrogen fertilisers (which among others applies to the production of nitric acid):

- Reduction of wastewater, resulting in a specific volume of wastewater of not more than 1 m<sup>3</sup>/ton N of the product, by:
  - application of closed cycles for recirculation of mother liquid or aqueous condensate into the synthesis process and
  - use of wastewater or aqueous condensate for other production processes (integrated industrial setup for wastewater) and
- Application of physical-chemical processes of wastewater clarification (sedimentation, neutralisation, stripping); utilisation or disposal of residues of the wastewater clarification separate to wastewater.

Table 15: Emission limits for the discharge of wastewater at the production of nitrogen fertilisers according to the AEV "anorganische Düngemittel"

	I) emission limits for discharge into running waters	II) emission limits for discharge into public sewerage
<b>general parameter</b>		
Temperature	30 °C	35 °C
fish toxicity $G_F$	4	no impairment of biological decomposition
filterable substances	30 mg/l	150 mg/l
pH	6.5–8.5	6.5–9.5
<b>inorganic parameter</b>		
$NH_4^+$ calculated as N <sup>1)</sup>	0.5 kg/t	0.5 kg/t
$NO_3^{-1}$	0.5 kg/t	0.5 kg/t
$NO_2^{-1}$	0.02 kg/t	0.02 kg/t
<b>organic parameter</b>		
CSB calculated as $O_2$ <sup>1)</sup>	0.5 kg/t	–

<sup>1)</sup> Emission values refer to the installed product capacity (as tons N of the product)

## 7.2 Germany

The regulatory order "TA Luft" contains the clean air regulations which have to be complied with by the authorising and controlling body. Under number 3 of "TA Luft", regulations concerning limits and determination of emissions are given. Regulations for nitric acid plants are specified under number 3.3.4.1a.1. According to TA Luft, version of 1986, the following regulations for the emissions of nitrogen oxides from nitric acid plants are in force. Old installations had to comply with the requirements by 1 March 1996.

- Emissions of nitrogen monoxide and nitrogen dioxide in the waste gas must not exceed  $0.45 \text{ g/Nm}^3$  (as nitrogen dioxide)
- Waste gases have to be discharged colourlessly; this is as a rule ensured if the mass concentration of nitric dioxide in the waste gas does not exceed the value resulting from the following equation:

$$\text{mass concentration of } NO_2 \text{ [mg/Nm}^3\text{]} = \frac{1200}{\text{inside diameter of stack orifice (dm)}}$$

Within an amendment of TA Luft emission limits will be updated in order to meet requirements according to EC-regulations and the BImSchG (Bundesimmissionsschutzgesetz). By this amendment most of the industrial installations will be concerned [LANGE, 2001].

### 7.3 Protocol to the 1979 Convention on Long-range Transboundary Air Pollution to Abate Acidification, Eutrophication and Ground-level Ozone

Annex V of the protocol to the 1979 convention on long-range transboundary air pollution to abate acidification, eutrophication and ground-level ozone contains limit values for the emissions of nitrogen oxides from selected stationary sources ([http://www.unece.org/env/lrtap/multi\\_h1.htm](http://www.unece.org/env/lrtap/multi_h1.htm)). The Protocol is currently not in force (16 ratifications are needed).

These sources include nitric acid production. The corresponding limit values are summarised in Table 16.

*Table 16: Limit values for NO<sub>x</sub> emissions released from nitric acid production excluding acid concentration units*

Capacity, technique, fuel specification	Limit value (mg/Nm <sup>3</sup> )
New installations	350
Existing installations	450

## 8 MONITORING OF EMISSIONS

Continuous measurement of nitric oxides ( $\text{NO}_x$ ) is state-of-the-art technology. At Austrian nitric acid plants  $\text{NO}_x$ -emissions are measured continuously. Current  $\text{NO}_x$ -emission values are available to the local authority online.

Continuous measurement of nitrous oxides ( $\text{N}_2\text{O}$ ) is state-of-the-art technology. At Austrian plants, emissions of  $\text{N}_2\text{O}$  are measured continuously. Emission values are not forwarded online to the local authority.

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