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NOVEL CATALYTIC PROCESS FOR FLUE GAS CONDITIONING IN ELECTROSTATIC PRECIPITATORS OF COAL-FIRED POWER PLANTS

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Problem formulation

- Coal-fired power generation capacity in the world is about 44% of the total electricity generation, in Europe – 42%, in Russia – 20%

- Coals used on power plants contain from 7wt% – 14wt% to 40wt% – 50wt% of flying ash

- A lot of such power plants are equipped with electrostatic precipitators (ESPs) for control of particulate matter (PM) emissions from

- The most part of flying ashes formed at coal burning in power plants possess unfavorable electrophysical properties

There is great value in increasing the efficiency of ESPs by lowering the resistivity of fly ash
Flue gas conditioning concept

ESP upgrade technique for decrease of ash resistivity

- Injecting small concentrations (2 - 10 vppm) of SO$_3$
- The surface absorbed SO$_3$ effectively increase electrical conduction of the bulk fly ash

Controlled catalytic oxidation of SO$_2$ may be a cost-effective upgrade to condition the flue gas for improved ESP performance

\[ \text{SO}_2 + \frac{1}{2} \text{O}_2 \rightarrow \text{SO}_3 \]

Possible feedstock

- SO$_2$ contained in flue gases (typically 200 - 300 vppm)
- External SO$_2$ sources (vessels, liquid SO$_2$, elemental sulfur)
Possible process flow-sheets

1. Oxidation of $\text{SO}_2$, present in the flue gases of coal-fired boilers, directly in the media of flue gases: 1a, 1b, 1c, 1d

2. Oxidation of $\text{SO}_2$ in separate stream with high concentration of $\text{SO}_2$
Preliminary selection of catalysts

+ good catalytic properties
+ few decades of successful industrial experience
+ low price, unlimited market availability
- low activity at low temperatures and at low SO$_2$ content
- not produced in structured form (high pressure drop, not applicable in dusty flows)

+ excellent activity at low temperatures and at low SO$_2$ content
- high price, very limited market availability
- not produced in structured form (high pressure drop, not applicable in dusty flows)

+ wide temperature window of efficient operation
+ possibility to form structured packings, applicability in dusty flows
+ moderate price, market availability is currently limited, but may be expanded
- limited industrial experience, requires additional research

Vanadium pentoxide
Sibunit carbon
Glass-fiber
### Calculation results

**Case study: typical Russian 300 MW boiler TPP-210A fed by Kuznetsk coal**

(flue gas flow rate 1.2 mln.m³/hr; required SO₃ content – 10 vppm; low-temperature zone 160°C; high-temperature zone 430°C; SO₂ content – 250 vppm; maximum additional pressure drop – ~ 50 mm WC)

<table>
<thead>
<tr>
<th>Case</th>
<th>Catalyst</th>
<th>Required level of SO₂ conversion, %</th>
<th>Flue gases flow rate in the catalyst bed, st.m³/hour</th>
<th>Required catalyst loading, m³ (ton)</th>
<th>Cost of unit catalyst loading, USD</th>
<th>Catalyst bed pressure drop, mm WC</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>Sibunit, granular</td>
<td>4</td>
<td>1200000</td>
<td>330 (200)</td>
<td>5’000’000</td>
<td>&gt; 3000</td>
</tr>
<tr>
<td>1b</td>
<td>Sibunit, granular</td>
<td>100</td>
<td>48000</td>
<td>27 (16)</td>
<td>400’000</td>
<td>&gt; 1000</td>
</tr>
<tr>
<td>1c</td>
<td>V₂O₅/SiO₂, granular</td>
<td>4</td>
<td>1200000</td>
<td>233 (180)</td>
<td>900’000</td>
<td>&gt; 2000</td>
</tr>
<tr>
<td>1d</td>
<td>V₂O₅/SiO₂, granular</td>
<td>100</td>
<td>48000</td>
<td>30 (24)</td>
<td>120’000</td>
<td>&gt; 1000</td>
</tr>
<tr>
<td>1c’</td>
<td>Glass-fiber catalyst</td>
<td>4</td>
<td>1200000</td>
<td>160 (20)</td>
<td>600’000</td>
<td>~ 250</td>
</tr>
<tr>
<td>1d’</td>
<td>Glass-fiber catalyst</td>
<td>100</td>
<td>48000</td>
<td>24 (8)</td>
<td>240’000</td>
<td>~ 150</td>
</tr>
<tr>
<td>2*</td>
<td>Glass-fiber catalyst</td>
<td>78</td>
<td>155</td>
<td>0.05 (6.6*10⁻³)</td>
<td>180</td>
<td>Not important</td>
</tr>
</tbody>
</table>

**Calculation results**

- Liquid sulfur consumption 22 kg/hour (176 ton/year) or 5’300 USD/year.

- In-duct oxidation with sibunit and vanadium catalyst excluded from consideration
- By-pass in-duct oxidation with fiber-glass catalyst may be considered

**The choice of route 2 (separate stream oxidation) is obvious**

Possible catalysts – vanadium or Pt/Glass-fiber
Glass-fiber catalysts (GFC)

Preliminary synthesis:
19 different samples on silica and Zr-silica glass-fiber supports with various fabric texture, Pt and $V_2O_5$ as an active components

While in conventional catalysts the noble metals (Pt, Pd, etc.) are usually present in form of metal particles, in case of GFCs the metal is incorporated in the fiber bulk
**Laboratory tests**

The scheme of experimental installation for catalysts testing:

1 – SO₂; 2 – O₂; 3 – He; 4.1, 4.2, 4.3 – manometers; 5.1, 5.2, 5.3, 5.6-7, 5.6-8 – shutoff valves; 6 – gas separation block; 7.1, 7.2, 7.3 – flow-mass controllers; 8 – gas preparation block; 9.8-12, 9.8-19 – flow rate regulators; 10 – gas mixing block; 11, 17 – pneumatic six-canal gas samplers; 12 – thermostatic box; 13 – reactor heater; 14 – reactor; 15 – box; 16 – SO₃ trap; 18 – foamy flowmeter; 19 – chromatograph; 20 – He pipe; 21 – sorbent pipe; 22 – exhaust.

- **Testing conditions:** catalyst loading – 0.17 g;
  - gas mixture: SO₂ – 1.67%, O₂ – 3.33%, He – 95%;
  - gas flow rate – 51 ml/min;
  - contact time – 0.3-0.5 sec;
  - temperature range 300°C – 550°C

- **Catalyst samples:**
  - 7 of GFC (with Pt and V₂O₅),
  - 1 of granular vanadium IC-1-6,
  - 1 of mixed (IC-1-6 + Pt/GFC)
Glass-fiber catalysts activity tests

- Catalysts based on silica glass-fibers excluded from consideration due to their insufficient thermal stability.
- Pt samples on Zr-silica glass-fibers demonstrate generally higher activity than $V_2O_5/Zr$-silica GFC’s.

**Paradox:**
the sample with lower Pt content shows higher activity than the sample with higher Pt content.

**Explanation:**
ionic form of platinum is dominating in the sample with low Pt content, while in the sample with higher Pt loading such domination belongs to metallic platinum.
Comparative catalyst activity tests

Conventional vanadium catalyst IC-1-6 demonstrate excellent high-temperature activity, while Pt/GFC is characterized with better low-temperature performance.

Combined catalytic system, containing structured mixture of granular V₂O₅ catalyst and Pt/FGC fabric (1:1 in mass) demonstrate combination of advantages: good performance both at low and high temperatures.
Optimal solutions for flue gas conditioning

- **Optimal process**: SO$_2$ oxidation in separate stream with injection of produced SO$_3$ into main gas duct before ESP

- **Optimal catalyst**: structured combination of granular conventional vanadium catalyst with Pt/GFC

- **Optimal injection**: uniform distribution of SO$_3$ at the inlet of ESP section required for efficient conditioning may be provided by proper design of the injecting device

- **Keynote factor**: operating efficiency and reliability of SO$_2$ oxidation reactor
Pilot tests

- site – Biysk Oleum Plant (Biysk, Altai region, Russia)
- design pilot unit capacity (for reaction mixture) – up to 120 st.m³/hour
- initial SO₂ content – 6-8% vol.
- SO₃ productivity – ~ 3 st.m³/hour

The external appearance

The pilot unit scale is practically equal to real capacity, required for conditioning of flue gases of full-scale power plants with 100 MW boiler and flue gas flow rate of 0.4 mln.st.m³/hour

The scheme of reactor

Description:

1, 2 – inlet and outlet gas flows; 3, 4, 5 – thermocouples for gas temperature measurements at reactor inlet, middle and outlet; 6, 7 – large and small catalytic cartridges; 8, 9 – sampling sockets for inlet and outlet gas; 10 – ceramic packing for improvement of flow distribution; 11, 12, 13 – metal gauzes for 10, 6 and 7; 14 – cross-piece for separation of cartridges and for installation of 12 and 4; 15 – mineral wool; 16 – supporting arms for gauze 13; 17 – U-type manometer; 18 – reactor cowling; 19, 20 – bottom and upper reactor lid.
Catalytic cartridges

The structure and the appearance of the composite catalytic cartridges for pilot unit developed and created in BIC, Russia

Commercial vanadium catalyst IC-1-6

Structure-forming metal gauze

Platinum fiber-glass catalyst
Startup heating. Ignition temperature

Observed "ignition" temperature is sufficiently lower than that for most of known commercial vanadium catalysts (~410°C - 420°C)

"Ignition" point of the composite catalytic cartridge is about 380°C - 385°C
Resource tests

Optimal conditions:
gas flow rate – 100 st.m³/hour,
inlet gas temperature –
400°C - 410°C

Differences between inlet and outlet
gas temperatures for each catalyst
bed (cartridge) during the resource
tests

1-st cartridge: gradual decrease of the temperature difference in the first half of the tests, then it stabilizes

2-nd cartridge: stable positive temperature rise in the first half of the tests, then it sharply drops
Resource tests

The rather significant data scattering – result of oscillations of inlet gas external parameters (temperature, flow rate, $SO_2$ concentration)

However, in general, some trend conversion decrease in time is seen.
The “ignition” temperature is at the level of ~380°C – the same value obtained for the fresh combined catalytic cartridges in the beginning of pilot tests.

**Preliminary conclusions:**

- Catalytic properties of the Pt/GFC – not changed sufficiently
- Partial deactivation of vanadium catalyst – may be
Final laboratory check of catalysts

After more than 1000 hours of pilot tests

Pt/GFC: no decrease of activity was found at all, even some activation is seen

Traditional vanadium catalyst:
significant deactivation, especially at low temperatures

Vanadium catalyst deactivation may be avoided in future by simple improvement of reactor design with minimization of heat losses to environment

General conclusion: Pt/GFC catalyst demonstrates stable and efficient performance, the pilot tests have successfully confirmed the efficiency of the proposed technology for SO$_3$ production
Conclusions

✓ The new technology for controlled SO₃ production for conditioning of flue gases from coal-fired power plants was proposed.

✓ The combined catalytic system consisting of the novel platinum catalyst on the base of silica-zirconium glass-fiber supports and conventional vanadium catalyst was developed.

✓ The pilot tests have demonstrated reliable and stable operation of the combined catalytic system characterized with high activity, low “ignition” temperature and practical absence of Pt/GFC deactivation.

✓ The developed technology may be recommended for industrial application without further scale-up.
Acknowledgements

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Thank You for attention ☺️