Nickel Carbonyl - are you sure your company knows how to avoid it, detect it and treat its effects?

In an ammonia plant reformers and methanators contain nickel-containing catalysts, which are exposed to carbon monoxide containing gas. This paper aims to help you manage the potential hazard that results from these two facts. Nickel carbonyl is an extremely toxic substance that can be readily formed when carbon monoxide comes in contact with nickel at the appropriate conditions. Nickel carbonyl formation is a chemical hazard that can be easily overlooked as part of the plant process controls for Safety & Health assessment as it not part of the main process. A number of previous incidents involving ammonia and methanol plant operations where operators have been seriously injured/affected by exposure are reviewed and the best practice for avoiding nickel carbonyl formation is described. Experience from other industries that deliberately produce nickel carbonyl is also included. This paper serves as a timely reminder of some of the less familiar hazards of running a chemical plant.

Tim Abbott
Johnson Matthey Catalysts

Keith Lascelles
Formerly of Vale Inco

Introduction

You may have noticed in your catalyst supplier’s product information, for example in a MSDS, about how it is possible to make nickel carbonyl from nickel based catalysts and carbon monoxide. This doesn’t happen under normal operating conditions but it can happen under abnormal conditions, during process upsets, start-up or shutdown. At these times, the possibility of making nickel carbonyl is probably right at the back of your mind. The intention of this paper is to bring it to the front of your mind, because nickel carbonyl is a dangerous substance. It is highly toxic and flammable, and can be difficult to detect. As several plant operators have found, disposing of nickel carbonyl can be costly and time consuming. The best tactic with nickel carbonyl is simple; don’t make any by avoiding conditions under which it can be formed.

This paper will give you:
- Information on the properties of nickel carbonyl and its hazards.
- Information on the conditions under which it forms, including syngas plant examples.
- Guidelines on how to avoid these conditions.
- Guidelines on how to detect and dispose of nickel carbonyl if you do form it.

You may need to check your start-up and shut-down procedures, and check that you have an action plan and the appropriate information to hand should you suspect that you have made nickel carbonyl.
History and uses of nickel carbonyl

Although in syngas plants nickel carbonyl is a potential hazard it is an important chemical used in large quantities in the production of high purity nickel.

Nickel carbonyl was discovered in 1889 by Ludwig Mond and co-workers. It is a highly volatile liquid, boiling point 43°C (109°F), and is formed from nickel and carbon monoxide.

\[ \text{Ni} + 4\text{CO} \rightleftharpoons \text{Ni(CO)}_4 \]

At atmospheric pressure, the forward reaction takes place at low temperatures, less than about 100°C (212°F). The reverse reaction takes place above about 180°C (356°F). It was initially a chemical curiosity, among the first compounds of a metal that could exist as a gas at ambient conditions. The discovery of other transition metal carbonyls followed, for example iron pentacarbonyl, Fe(CO)_5. Mond, however saw the potential of the nickel carbonyl reaction to refine nickel, reacting impure nickel-bearing materials with carbon monoxide to form nickel carbonyl, and decomposing it to form pure nickel, recycling the carbon monoxide.

After pilot work, the world’s first carbonyl refinery began at Clydach, in South Wales in 1902, and is still operating as part of Vale Inco. This refinery operates at atmospheric pressure. There is now also a Vale Inco refinery in Sudbury, Ontario as well as Norilsk refinery in Russia and a smaller plant in China. The main products from these plants are high purity nickel pellet and nickel powder; although it is possible to produce other nickel-coated products, for example nickel coated graphite. Tens of thousands of tonnes of nickel are produced by the carbonyl process each year with many uses; pellet in stainless steel and other nickel alloy production and in electroplating; powder in battery production.

Given the potential hazards of nickel carbonyl, the industry has developed robust operations and engineering to handle the material. Any waste gases containing nickel carbonyl are incinerated, collecting the nickel oxide dust formed, and there is extensive testing and atmospheric monitoring so that any leaks can be detected and dealt with promptly.

Chemistry of nickel carbonyl formation

Nickel carbonyl Ni(CO)_4 can form when a reduced metallic nickel surface is exposed to a gas atmosphere containing carbon monoxide under certain temperature and pressure conditions. In general, its formation is favoured by low temperature and high pressure.
The following equilibrium relationship derived from thermodynamic data is generally considered to be reliable:

For the reaction \( \text{Ni} + 4\text{CO} \rightleftharpoons \text{Ni(CO)}_4 \)

\[
\log_{10} K_p = \frac{8546}{T} - 21.64
\]

where \( T \) is the temperature in degrees Kelvin. Pressure in atmospheres.[1]

Figures 1 to 3 show the equilibrium curves for \( \text{Ni(CO)}_4 \) at a range of pressures, CO concentrations and temperatures.

Figure 1 – Nickel carbonyl equilibria. Pressure = 1 atm

Figure 2 – Nickel carbonyl equilibria. Pressure = 5 atm
The equilibrium amount of nickel carbonyl is strongly temperature dependent. For example if part of a catalyst bed is twenty degrees cooler than the point of measurement, you could make ten times as much nickel carbonyl.

Thermodynamics tell you the amount of nickel carbonyl that is formed at equilibrium, in effect the maximum amount. In the absence of any detailed information on the kinetics of its formation, the safest assumption is that you will form the equilibrium amount of nickel carbonyl. The main justification for this is that although the reaction is slow in molecular terms (1.2 x 10^{-4} mole/m² min for polycrystalline nickel in pure CO at atmospheric pressure at 120°C), nickel catalysts have a high surface area of nickel, well in excess of 1m²/g. As most catalyst beds contain tonnes of nickel then the surface of nickel available can be many thousands of square metres.

It has been reported that nitrogen produced in plants close to busy highways or CO plants can contain up to 100ppm of CO. The equilibrium diagrams show that at one atmosphere, this can form ppb levels of nickel carbonyl. This is not likely to be a health hazard to personnel – if you breathe the gas you are more likely to suffer from lack of oxygen, or even the effects of the CO. However it could cause a problem if the nitrogen was being used to purge plant equipment containing trace levels of nickel carbonyl.

Just as the formation of nickel carbonyl is governed by equilibrium, so is its decomposition. If, for example, the equilibrium amount of carbon monoxide is removed in some way, then the nickel carbonyl will tend to decompose to nickel and carbon monoxide, albeit slowly at ambient temperature.

Nickel carbonyl also decomposes in air at ambient temperatures, the main products being nickel oxide and carbon dioxide.
Properties of nickel carbonyl

Table 1

<table>
<thead>
<tr>
<th>Substance</th>
<th>Nickel carbonyl (tetracarbonyl nickel) CAS 13463-39-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula M Wt</td>
<td>Ni(CO)₄</td>
</tr>
<tr>
<td></td>
<td>170.3</td>
</tr>
<tr>
<td>Physical properties</td>
<td>Colourless liquid</td>
</tr>
<tr>
<td></td>
<td>B. Pt. 43°C (109°F), M. Pt. –25°C (-13°F)</td>
</tr>
<tr>
<td></td>
<td>Very slightly soluble in water (0.0018g/100 ml at 20°C/68°F)</td>
</tr>
<tr>
<td>Odour</td>
<td>Sooty odour detectable at 0.5 to 3 ppm</td>
</tr>
<tr>
<td>Vapour density</td>
<td>5.89 (air = 1.0)</td>
</tr>
<tr>
<td>Vapour pressure</td>
<td>321 mmHg at 20°C (68°F)</td>
</tr>
<tr>
<td>Flash point</td>
<td>&lt;20°C (-4°F)</td>
</tr>
<tr>
<td>Auto-ignition temperature</td>
<td>Explosive above 60°C (140°F)</td>
</tr>
<tr>
<td>Specific Gravity of liquid</td>
<td>1.31</td>
</tr>
</tbody>
</table>

The specific properties of nickel carbonyl have some practical implications:

- Its high vapour density relative to air means that the vapour can gather in low spots.

- Its vapour pressure means that it is possible to condense liquid nickel carbonyl in cold spots. This can be a particular problem in a dead leg or tapping point, where subsequent purging at ambient temperature may not be very effective.

- The fact that liquid nickel carbonyl is denser than water and sparingly soluble in water means that it is possible to trap a liquid spill under water. For this reason Vale Inco’s liquid nickel carbonyl storage vessels are all above a water filled bund. In theory, the partial pressure of nickel carbonyl above the water will reach its vapour pressure; in practice, its passage through the water layer is slow. This has a further implication from the point of view of purging. If you have a water layer above the liquid nickel carbonyl, purging is almost ineffective.

Potential ways nickel carbonyl may be formed in your plant

There are a variety of abnormal conditions that may lead to nickel carbonyl formation in syngas plants. During normal operating conditions nickel carbonyl is simply not an issue due to high temperatures. As market leaders in syngas catalysis, including many nickel based catalyst products, Johnson Matthey Catalysts have close relationships with many customers operating units and we are often consulted regarding nickel carbonyl issues. Johnson Matthey ensures our product information clearly highlights the potential issues including information about nickel carbonyl in our operating manuals, raising the subject at our training seminars and ensuring our personnel are fully aware that incidents have occurred every few years since the 1960s. In this paper we highlight some of these examples. All are based upon real incidents but no references to the source or location of these examples are given.

For the formation of nickel carbonyl in an ammonia plant three key conditions must exist
- available reduced nickel
- carbon monoxide
- physical conditions.
Available nickel

Figure 4 - Potential nickel locations on a typical ammonia plant.

The main sources of available nickel are the hydrodesulphurization, pre-reforming, primary reforming, secondary reforming and methanation catalysts. The main catalysts types that incorporate nickel in order of typical nickel metal content are shown in table 2.
Table 2 – Typical nickel content of catalysts in an ammonia plant.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Typical Nickel Content % w/w</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-reforming</td>
<td>50</td>
</tr>
<tr>
<td>Methanation</td>
<td>30</td>
</tr>
<tr>
<td>Primary Reforming</td>
<td>20</td>
</tr>
<tr>
<td>Secondary reforming</td>
<td>10</td>
</tr>
<tr>
<td>Hydro-desulphurisation (Ni/Mo type)</td>
<td>5</td>
</tr>
</tbody>
</table>

It is not simply the nickel content that is important but the fact that these catalysts are designed and manufactured to maximize the surface of nickel area available to catalyse reaction. The micrographs in Figures 5 and 6 show the nickel surface of a primary reformer catalyst. If the nickel surface in one tonne of Johnson Matthey’s KATALCO JM 23-4Q steam reforming catalyst could be laid out flat then it would cover over 3000 soccer pitches.

Figure 5 - Micrograph of KATALCO JM 23-4Q at 2000 times magnification.

Figure 6 - Micrograph of KATALCO JM 23-4Q at 5000 times magnification.

Clearly with this entire nickel surface available any CO can react to give equilibrium concentrations of Ni(CO)₄.

There are other sources of nickel within a syngas plant but catalysts are the by far the most significant. Although nickel in pipework has been shown to be a potential source that may lead to formation of both nickel carbonyl and iron pentacarbonyl there appear to be no known incidents where substantial quantities of carbonyls have been formed in this way leading to risk to personnel.

This paper focuses upon nickel carbonyl but iron pentacarbonyl is also highly toxic and issues regarding both these carbonyls have been studied for many years. [3] The main area of concern with iron carbonyl within syngas plants is not the potential hazard from its toxicity but the poisoning of methanol synthesis catalyst. [4]

Available CO

Looking at scenarios where CO may be present leads to several possibilities on most designs of syngas plant as illustrated in Figures 7 to 12. Some of these are applicable to Methanol plants only because of the higher levels of CO in the methanol synthesis loop. The presence of a methanator to effectively eliminate CO from the ammonia loop significantly reduces the risk of CO being inadverently recycled to the front end of the plant. However that does mean the methanator itself, as described in the cases studies later, represents the biggest potential nickel carbonyl hazard.
Multiple reformers sharing common compressors with the potential of leaking valves. Any linkages between plants especially temporary modifications need careful review with respect to the potential for nickel carbonyl formation.

In a methanol plant flowsheet with the reformer off-line there is the potential for high CO containing gas to depressure back to the reformer. There is little risk in an ammonia plant where the CO level in any returning gas would be very low.
Physical conditions

Controlling of the physical conditions is the key to avoiding the formation of nickel carbonyl in a syngas plant.

Fortunately normal operating conditions of high temperature prevent nickel carbonyl being formed.

It is only during periods of operation at low temperature below about 200°C (390°F) that the issue may arise, that is start-up and shutdown conditions only.

Case history 1 – ammonia plant

As is often the case in syngas plants it was an unplanned plant shutdown that led to this incident, which occurred many years ago but still has lessons valid for today.

The plant was shut down due to an internal leak on the secondary waste heat boiler. The following actions were taken:

- ammonia loop shutdown
- methanator isolated and put under a positive nitrogen pressure
- low temperature shift by-passed
- process gas sent to flare system.

However the partial shutdown lasted longer than anticipated and the methanator cooled down to 25°C. It became necessary to fit a slip plate to complete some other essential maintenance work.

As a result, several personnel were exposed to nickel carbonyl with some requiring hospital treatment.

What led to this?

It was established that gas containing a high concentration of carbon monoxide (CO) leaked...
through the closed inlet isolation valve into the methanator.

Initially the temperature of the methanator, above 200°C (390°F), meant that decomposition of nickel carbonyl was favoured but as the temperature fell this was no longer the case. When the N₂ purge was stopped to allow a slip plate to be fitted in the methanator exit line the concentration of nickel carbonyl probably rose further because whilst the joint was being broken nitrogen was flowing but when the slip plate was being fitted nitrogen was not flowing allowing process gas to leak in to the methanator.

Consequently as soon as the joint was broken nickel carbonyl began escaping into the surrounding area, which continued until the slip-plated joint was tightened. Personnel were not wearing breathing apparatus, as the presence of toxic gas was not anticipated.

Analysis of samples taken from in the methanator showed nickel carbonyl in excess of 5000 ppm.

Since this event occurred this plant operator has carried out many reviews and actions to prevent re-occurrence of this or similar incidents on their site.

Figure 13 – Formation of nickel carbonyl

Case History 2 – ammonia plant

An ammonia plant was preparing to replace their methanator and decided to review operating data. Using plant data obtained, as the plant was being shutdown, they plotted the CO partial pressure in comparison to Johnson Matthey’s recommendations as shown in Figure 13.

The plant conditions (plotted in red) are initially in the area of the graph where formation of nickel carbonyl is not favorable before crossing over into the favorable region during the shutdown. So they were almost certainly forming nickel carbonyl during every shutdown. Fortunately the solution is straightforward – avoid the physical conditions where nickel carbonyl will form.

The precautions Johnson Matthey regards as best practice are as stated in our operating manual. We recommend that during a shutdown the methanator be purged with nitrogen while it is still above 200°C (390°F). Special care should then be taken to ensure that gases containing carbon monoxide do not leak into the vessel during cooling. If maintenance work is to be carried out the methanator should be isolated with slip plates by personnel wearing long line breathers.

During start-up the methanator should be heated at low pressures until the temperature is above 200°C (390°F). The warm-up gas should be flared.
and all local vents and drains checked to ensure that they are closed. Once the temperature is above 200°C (390°F) the pressure can be increased.

**Case History 3 – Ammonia Plant**

An ammonia operator was about to discharge methanation catalyst for replacement. On purging with nitrogen they measured several hundred ppb of nickel carbonyl. In attempting to purge with nitrogen further to reduce the nickel carbonyl concentration the concentration actually increased.

The likelihood is that during the time the purging was taking place the methanator was cooling and the equilibrium effect was driving up the concentration of nickel carbonyl.

The lesson is if you detect nickel carbonyl thinking carefully what steps will reduce or eliminate it.

**Responding to a nickel carbonyl incident**

It is not the intention of this paper to detail the response but to provide some outline information and encourage preparation and review of response plans. Key issues include the toxicity of nickel carbonyl, its unusual physical characteristics, detection and measurement, protection and exposure monitoring of employees.

Other references have gone into more detail in this matter. [2].

**Toxicity data**

The specified exposure limits for nickel compounds, including nickel carbonyl are set differently by different countries. In addition, they are revised from time to time, so it is essential to obtain up-to-date data. The best source of these is the NiPERA (Nickel Producers Environmental Research Association) Website (www.niper.org).

In the USA, the American Conference of Governmental Industrial Hygienists set a TLV (Threshold Limit Value) of 0.05 ppm for nickel carbonyl. This has been adopted by several countries, but the USA Occupational Safety and Health Administration have set an 8-hour time weighted average Permissible Exposure Limit of 1 ppb (0.001 ppm). This corresponds to 0.0024 mg/m³ of nickel as nickel carbonyl, or 0.007 mg/m³ of nickel carbonyl.

For comparison, the corresponding PEL for carbon monoxide is 50 ppm.

In the UK, the toxicity levels set by the Health and Safety Executive present a fuller picture.

**Table 4 – Toxicity levels as set by the Health & Safety Executive**

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<table>
<thead>
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<tbody>
<tr>
<td>8 hour long term exposure</td>
<td>No value set as safe</td>
</tr>
<tr>
<td>limit</td>
<td></td>
</tr>
<tr>
<td>15 minute STEL (STEL)</td>
<td>0.1 ppm</td>
</tr>
<tr>
<td>(Short Term Exposure Limit)</td>
<td></td>
</tr>
<tr>
<td>SLOT DTL (SLOD) (Specified Level Of Toxicity Dangerous Toxic Load)</td>
<td>150 ppm min</td>
</tr>
<tr>
<td>SLOD DTL (Significant Likelihood of Death Dangerous Toxic Load)</td>
<td>450 ppm min</td>
</tr>
</tbody>
</table>

The STEL is the maximum concentration of a chemical to which workers may be exposed continuously for up to 15 minutes without danger to health or work efficiency and safety.

The SLOD DTL refers more to a release affecting the general population. Such exposure would cause severe distress to almost everyone in the area, a substantial fraction of the exposed population requiring medical attention; some people se-
riously injured requiring prolonged treatment, and highly susceptible people being killed.

The SLOD DTL is in effect an LD50; 50% of exposed people would die.

Medical issues

The greatest danger to health from nickel carbonyl is from inhalation. It can be absorbed through the skin, it can affect the eyes, and it may be a carcinogen, but these present lesser dangers. The diagnosis and treatment of suspected nickel carbonyl poisoning must be in the hands of medical professionals, to whom full information is available. The following is for information only.

The initial symptoms of nickel carbonyl poisoning, lasting 12 to 36 hours, include a headache, dizziness and nausea. Delayed symptoms appearing 3 to 5 days later include chest pain, shortness of breath, a dry cough, weakness and a bluish colour of the lips.

Analysis of nickel in urine, taken at specific times, can confirm exposure and if appropriate Antabuse can be prescribed to assist in removing nickel from the system.

Protection

Respiratory protection to personnel must be by using a full-face respirator, either self-contained or with air from a central supply. Overalls and gloves provide skin protection.

How do you know if you’ve made nickel carbonyl?

As there are many different plant configurations and situations, we can only generalise.

- If you realise that you have had a gas containing carbon monoxide in contact with nickel catalysts under the low temperature conditions shown in figures 1-3, then you can assume that you have made some nickel carbonyl.

- Low levels of nickel carbonyl will colour a flare yellow. This is not a particularly reliable indication, as the flare may be yellow already, or be coloured yellow by other gases.

- Nickel carbonyl above ~0.1% will give a dust plume above a flare. Again, this is not a particularly reliable indication as the nickel carbonyl could be at lower levels, and other conditions can cause a flare to fume.

Many companies may already have in place an action plan to deal with the formation of nickel carbonyl. If not, the next steps are analysis to confirm the presence of nickel carbonyl (see below), then isolation of the contaminated section of plant, taking all precautions, prior to decontamination.

Detection and measurement of nickel carbonyl

There are only two analytical methods capable of measuring nickel carbonyl in air at the 1 ppb level prescribed in the USA. These are a chemiluminescence monitor, for example as manufactured by Ionics, or gas chromatography, requiring specific columns and an electron capture detector. Neither of these are normally immediately available.

More readily available methods to detect nickel carbonyl are:

- Draeger tubes. These cover the range 0.1 to 1 ppm

- Similar tubes supplied by the Gastech Corporation cover the range 10 to 200 ppm, or 200 to 800 ppm.

- Chemical analysis. Nickel carbonyl can be oxidised to $\text{Ni}^{2+}$ in solution with bromine,
chlorine or a source of chlorine such as sodium hypochlorite. Care is needed, as this can be a vigorous reaction. The nickel in solution can then be analysed by conventional solution analysis.

- Infra red spectrophotometry. Nickel carbonyl has a strong band at 2058 cm\(^{-1}\). 5 ppm can be measured using a 10 cm gas cell, or tens of parts per billion using a 20 m gas cell.

- Ultra violet spectrophotometry. Nickel carbonyl has a strong broad absorption peak in the UV at ~205 nm. High levels of CO interfere at this wavelength, but not above 220 nm. The absorption spectrum of iron carbonyl is virtually identical to that of nickel carbonyl. Sub ppm levels of nickel carbonyl can be measured using a 10 cm gas cell.

One of the methods used at Vale Inco to detect leaks of nickel carbonyl uses a modified butane lamp. The gas tested is sucked via a tubular probe into a butane flame. 2 - 3 ppm of nickel carbonyl colours the tip of the flame silver. This method can only be used where it is safe to use a naked flame.

**Disposal of nickel carbonyl**

The tactics adopted here will depend on the location and quantity of nickel carbonyl, and equipment available. The best overall philosophy is purging the contaminated equipment with CO-free nitrogen and decomposing the nickel carbonyl to nickel in a solid form that can be more readily handled and disposed of.[5]

The three main routes parallel what is used in the nickel industry; decomposition to solid nickel, decomposition to nickel powder, or incineration to nickel oxide. Note that all of these other forms of nickel are potentially hazardous to health. Plant personnel with experience of handling reformer catalysts should already be aware of the hazards of handling nickel oxide. Again, www.nipera.org gives information on maximum exposure levels.

Decomposition to solid nickel can be achieved by passing the nitrogen containing entrained nickel carbonyl through steel tubes packed with wire wool, and heated to 240 to 250°C. The wire wool increases the surface area available for decomposition, but can become blocked if the quantity of nickel-plated is large. The temperature is important. At too low a temperature or too high a gas flow rate the nickel carbonyl will not be completely decomposed. At too high a temperature, nickel powder will be formed, necessitating a filtration stage. The off gas will now contain small amounts of CO, and must be disposed of appropriately.

Decomposition to nickel powder requires a higher temperature, ~400°C, with filtration to catch the nickel powder formed, and disposal of the off gas.

There are two key points to remember when purging. Firstly, purge flows do not have to be high to be effective, and in fact high flows may complicate downstream decomposition. Secondly, because of the fact that nickel carbonyl can form as a liquid; deadlegs should be purged separately if possible. If not possible, deadlegs to low points should be heated to above the boiling point of nickel carbonyl to ensure complete vaporisation.

**Conclusion**

This paper has highlighted nickel carbonyl hazards and syngas plant operators should regularly review this topic.

In particular it is clear that a careful review of conditions during start-up and shutdown is worthwhile, many of you will have done this but when was it last re-visited?

The examples in this paper highlight that careful control of the physical conditions is an important
aspect of nickel carbonyl avoidance. The methanation stage in the ammonia process is the most important aspect to review but the potential hazard in the front end of all syngas plants has also been highlighted.

References