Hydrogen Explosion Incident of Leibstadt Nuclear Power Plant

Assessment of electrolysis risk in

immersion and jet-type electrode boilers

ZANDER & INGESTRÖM

ZETA Boiler USA LLC

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ZANDER & INGESTRÖM

1. Summary

Incident

In Aug 11th, 1995, an explosion occurred at Lebstadt NPP in Switzerland causing two injuries. The explosion occurred at the aux steam system where jet type electrode boilers were employed. Upon further investigation, it was identified that appx. **13ppm** of hydrogen was inside the boiler before the explosion occurred.

Findings/Analysis

One of Z&I's customers in Mulheim Germany was concerned about his immersion electrode boilers having similar risk. We performed theoretical research and testing and our findings indicate that immersion boilers, due to much lower current density, have hydrogen concentration in the boiler at around **60ppb** and generate hydrogen at 20 times lower rate than jet type boilers due to low current density in immersion boilers.

Recommendations

Since hydrogen production rate for immersion electrode boiler is in the order of ppb level, the explosion risk for immersion electrode boilers is much less than jet type electrode boilers. We urge that the specification for H_2 production rate be set to no more than 200 ppb. This not only reduces hydrogen explosion risk, but also minimizes corrosion from O_2. Out of precaution, Z&I has such a timed venting device to eliminate the risk of hydrogen explosion completely.

We urge any users of jet type electrode boilers to be aware of such risk and implement timed venting to purge any accumulated hydrogen in the system. This risk is much elevated in closed system (such as in HW set up where the steam is repeatedly recondensed). Hydrogen, along with oxygen will accumulate similar to what occurred in Leibstadt. Since oxygen will be generated, additional oxygen scavenger should be added to avoid accelerated corrosion.

2. Incident Background

On August 11, 1995, at 8:22 a.m, an explosion occurred at the Leibstadt Nuclear Power Plant (NPP) during maintenance work. Two employees sustained third - degree burns. The mechanics were conducting inspections in the engine section of the auxiliary steam system. When they opened the lid of a container, hydrogen escaped and ignited. Under normal operating conditions, the steam present in the affected system is from the reactor and thus contaminated. However, the accident did not occur in the nuclear part of the plant.

Link of original details:

http://de.wikipedia.org/wiki/Kernkraftwerk_Leibstadt

Accidents

Cooling Tower

Total intake of the power plant

On 11 August 1995, at 8:22 clock in the morning, took place in the NPP Leibstadt during the revision work in an explosion. Two employees suffered third degree burns. The mechanics were reviewed in the engine part of the auxiliary steam system. They opened a container of a lid, it came out of hydrogen, which is inflamed. In normal operation, located in the affected system steam that comes out of the reactor and is therefore contaminated. The accident did not take place in the nuclear part of the plant. [2]

On 28 March 2005 the plant was shut down due to a ground fault of the transformer. [3] The ground fault on the generator transformers damaged. During the early revision, there was a breakdown of the INES level 1 [4] It was only on 2 September was back to the plant network [5]

In 2007, the NPP Leibstadt the federal nuclear authority had to notify the three "incidents". While two of the incidents were classified by the regulator, the Department of Nuclear Safety Inspectorate (HSK), an event with little or no safety significance, it classified the reactor trip due to faulty triggering of the automatic pressure reducing system on 6 March 2007 at the International Event Scale INES at level 1 as a disturbance, namely a deviation from the permitted areas for the safe operation of the plant. [6] [7]

Link of hydrogen explosion information:

http://www.ecology.at/nni/index.php?p=site&s=167

1995-08-11

Hydrogen explosion in the turbine hall during refueling outage. 2 maint. workers from ABB incurred third degree burns.

3. Our Involvement

After this incident, RWE Energy, which is one of the largest electricity and natural gas companies in Germany, the country's largest power generation company and the largest renewable energy company, and operator of the Mulheim Karlich Power Plant. RWE contacted our representative (Klopper Therm GMBH) in Germany to ask Z&I to verify that the production of oxyhydrogen in ZETA Electrode Boiler will not be a reason for an explosion. And They need more information about the specific current load (watt density). Z&I conducted a detailed analysis and data collection to verify this matter.

3.1 Letter from RWE – English Translation

RWE Energie
AKTIENGESELLSCHAFT

Mülheim-Kärlich Power Plant

FAX

Mailbox 14 32
56210 Mülheim-Kärlich
Phone (02637) 64-1
Fax (02637) 64-2260

Fax No.: 0231/5178333

Name: H. Sanders — Phone: 5178-0

Firm: Klopper-Therm Gmbh — Department:

Address: 44022 Dortmund-Wambel

Name: Becker, Lothar — Phone: -2171

Department: TA

Message: KMK- Deflagration of Flammable Gases

Dear Mr. Sanders,

Due to an industrial accident caused by the explosion of hydrogen (H_2) in a Nuclear Power Plant, we ask you to check whether the following procedure also applies in our auxiliary steam boiler due to plant and process engineering.

In the power plant mentioned above, steam is generated in electrode steam boilers by introducing electrical energy (alternating current). The boiler shell serves as the cathode, the anode is a central pipe from which the electrical current flows through the water jets.

Clarifications from the boiler supplier have shown that a production of approx. 13 ppm H_2 occurs.

Depending on the steam output, approx. 3 m^3 H2 gas per day is discharged into the steam stream.

Page: 1 — Date: 1995-10-05

RWE Energie
AKTIENGESELLSCHAFT

Mülheim-Kärlich Power Plant

FAX

Mailbox 14 32
56210 Mülheim-Kärlich
Phone (02637) 64-1
Fax (02637) 64-2260

Page：2

To： Herrn Sanders

From：Klopper-Therm Gmbh，Dortmund – Wambe1

Fax No.： 0231/5178333

When the welded sealing disc on the upper manhole was unscrewed, an explosion occurred, causing burns to two workers.

Please notify us of the result of your review as soon as possible.

Kind Regards,
Gez Becher

3.2 Original letter from Klopper to Z&I

Our rep, Klopper-Therm then faxed Z&I this request to clarify the hydrogen production rate and to assure the safe operation of the ZETA Boiler.

TELEFAX - MITTEILUNG -
TELEFAX - MESSAGE

KLÖPPER THERM

Klöpper-Therm GmbH & Co.
Unterste-Wilms-Str. 19a D-44143 Dortmund-Wambel
Postfach 102263 D-44022 Dortmund
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Klöpper-Therm GmbH & Co.
Postfach 102263 44022 Dortmund
Unterste-Wilms-Straße 19a 44143 Dortmund (Wambel)
Telefon (0231) 5178-0 Telefax (0231) 5178-333

An	: Zander & Ingeström S-10223 Stockholm	Von	: Sanders
		Direkt-Tel.:	-326
z. H.	: Mr Rolf Hedenstedt	Datum	: 20.11.1995
Fax-Nr.:	0046 8 806567	Seite	: 1 von 4

Eccident in Leibstadt
Bayernwerk AG, ISAR 2

Dear Mr Hedenstedt,

some weeks ago we informed you about an eccident in Leibstadt (Switzerland). During opening a steam generarator oxyhydrogen, produced by an Sulzer Boiler, exploded. Two people has been hurt.

Now the people in german nuclear power plants has to verify that the production of oxyhydrogen in ZETA Electrode Boiler will not be a reason for an explosion.
We have talked to the people and gave them some information about production of oxyhydrogen in Electode boiler (see attachment).

But for ISAR 2 this information is not enough. They need moor information about the specific current load (watt density).
We discussed this problem with Mr Sahl during a phone call. He gave me the value of appr. 0,13 A/cm² for the specific current load.

Now the people from ISAR 2 would like to know the following:
- number of elektrode bundles
- number of elektrodes of each bundle
- surface of the electrodes
- specific current load at
  - full power
  - half power
  - stand by

We hope you can help us

kind regards
Klöpper - Therm GmbH & Co.

A. Sanders

Kommanditgesellschaft, Dortmund HRA 12322 AG Dortmund
Komplementärin: Klöpper-Therm Verwaltungs-GmbH, HRB 8600 AG Dortmund
Geschäftsführer: Alfred Beimdick, Friedrich Hinz, Walter Mälschner

Dresdner Bank AG (44080050) 1066316
Deutsche Bank AG (44070050) 1514587
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4. Analysis and data from Zander & Ingestrom Sweden

4.1 Analysis

Regarding water splitting and magnetite formation in steam boilers type ZDKI

When a direct current flows through water, part of the water is split into oxygen and hydrogen according to $H_2O>2H_2+0_2$. If you use alternating current instead of direct current, the same splitting takes place during half the period and during the other half of the period, the gases are reunited to water again.

In a steam boiler, some of the water turns to steam and therefore the re-combination to water is not complete. In an ordinary hot water or hot water boiler, we do not have the same problem. Measurements have been made on 2x35 Mw hot water boilers, but no measurable amount of gas were obtained. Other reports indicating water splitting have not been received either. The amounts of gas that are formed in a steam boiler are very small - that's why they have not been noticed before. The circuits in which we now have problems are so-called closed systems. There, an accumulation of the gases takes place and eventually an unacceptable level is reached. In an open system the steam is consumed and since the H_2 gas is fully "soluble" in the steam and its condensate, you don't get any accumulation in these systems. All condensate that goes back must of course be degassed.

According to measurements made, the amount of H_2 gas that are formed are 1-3 ppb ($1\text{-}3 \cdot 10^{-9}$).
The maximum amount of hydrogen that can be accepted in the circuit is 4.5% by volume.
Under normal conditions, the hydrogen gas in the circuit is harmless. Cracking gas consists of 2 parts by volume H_2 and 1 part by volume 0_2. The oxygen gas in the circuit disappears in the form of oxidation and does not accumulate, which is why cracking gas cannot be formed in sufficiently large quantities during operation. Oxygen can be reduced with, for example, hydrazine.
If the circuit cools down and sucks in air, you get new oxygen in again and the risk of explosive gas or combustible gas exists again.

Air containing more than 4.1% hydrogen burns, therefore the hydrogen content must be kept below 4.1%.

The oxygen gas, which is formed in the boiler through water splitting, is 8 times greater than the amount of hydrogen, thus 8-24 ppb. The damage it causes is partly pure corrosion, partly the oxygen lowers the pH value of the boiler water, steam and condensate.
The magnetite, which is an oxidation product, causes problems in the boiler, for example unnaturally high wear on the boiler circulation pump.

4.2 Data:

- *Equations for Hydrogen & Oxygen Production in AC Electrolysis*

The following equations describe the relationship between current density and gas evolution rates for hydrogen and oxygen production in water electrolysis under alternating current (AC).

- *General Form of the Equation*

The gas evolution rate (q) in $cm^3/cm^2/min$ follows a power-law relationship:

$q = k \cdot J^n$

where:

- q = gas production rate ($cm^3/cm^2/min$)

- J = current density (A/cm^2)

- k = empirical proportionality constant (adjusted for AC inefficiencies)

- n = empirical exponent based on electrolysis behavior

- *Hydrogen Production Equation*

Since AC electrolysis has inefficiencies due to polarity switching, hydrogen production is lower than in DC electrolysis. The equation used is:

$H_2(J) = 0.7 \times (0.14 \cdot J^{1.2})$

where:

- The factor '0.7' accounts for 'AC electrolysis efficiency loss' (~70% of DC efficiency).

- '0.14' is an estimated proportionality constant from experimental data.

- '1.2' is the exponent describing the nonlinear increase with current density.

- *Oxygen Production Equation*

Since oxygen is produced in a '2:1 ratio' with hydrogen in water electrolysis, the oxygen production follows:

$O_2(J) = H_2(J) / 2$

which simplifies to:

$O_2(J) = 0.5 \times (0.7 \times 0.14 \cdot J^{1.2})$

or:

$O_2(J) = 0.07 \cdot J^{1.2}$

Final Equations:

Hydrogen Production:

$H_2(J) = 0.098 \cdot J^{1.2}$

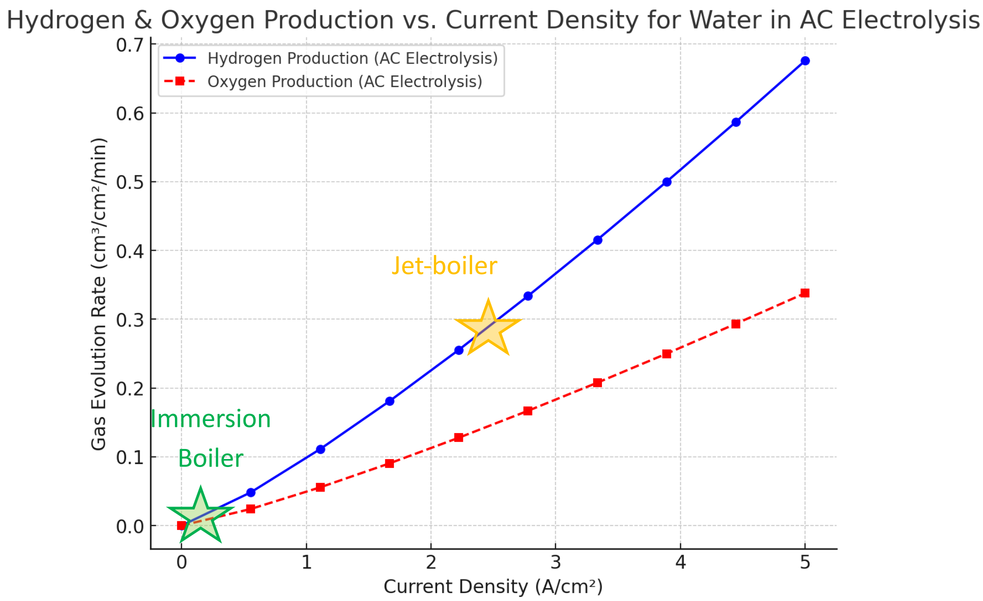
Oxygen Production:

$O_2(J) = 0.07 \cdot J^{1.2}$

J = current density (A/cm^2)

H_2/O_2 results with unit of $cm^3/cm^2/min$

These equations describe the "hydrogen and oxygen evolution rates" as a function of "current density in AC electrolysis". Further refinements may be needed for experimental validation.



Jet-boiler current density: ~2.5 A/cm^2 and produces hydrogen at 20 times the rate of immersion boilers

Immersion-boiler current density: ~0.15 A/cm^2

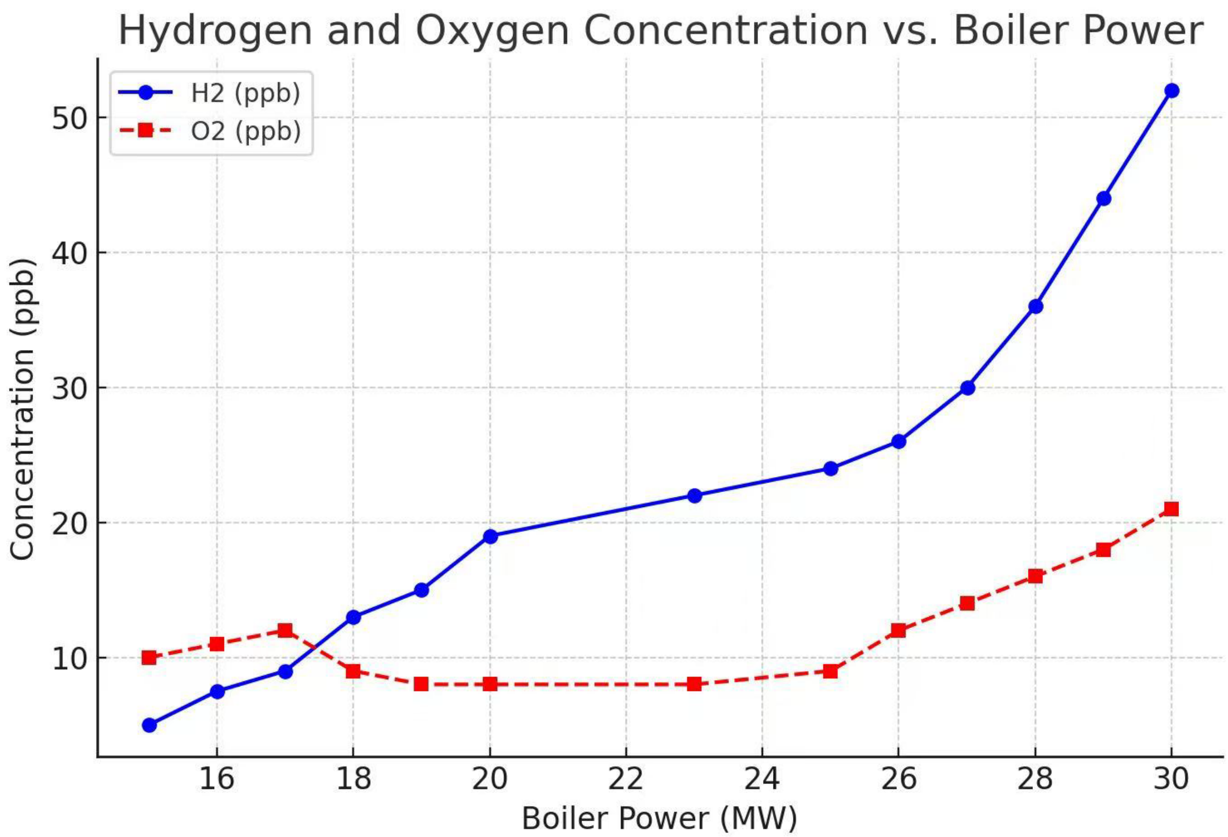
4.3 Hydrogen Measurement Record

Z&I conducted the measrements of H_2 and O_2 in ZETA boile gas. Records as below:

Gas Measurements 830617						
Time	Boiler Power MW	Level Inner Vessel	µs/cm Inner Vessel	H_2 ppb	O_2 ppb	Boiler Pressure bar
12:00	15	78	42	5	10	26
13:00	16	78	42	7,5	11	26
13:30	17	79	42	9	12	26
14:00	18	80	42	13	9	26
14:30	19	51	73	15	8	26
15:00	20	51	73	19	6	26
15:30	23	51	75	22	8	26
16:05	25	42	100	24	9	26
16:30	26	41	100	26	11	26
17:00	27	40	100	30	14	26
17:30	28	40	100	36	16	26
18:00	29	66	110	44	18	26
19:00	30	66	110	52	21	26
Boiler type		**Power MW**		**Voltage KV**		
Closed system YES NO			Open system YES NO			Steam
			Gas Measurements			
ZANDER & INGESTRÖM				Drawing NO. P-47328		

Gas Measurements 830615						
Time	Boiler Power MW	Level Inner Vessel	µs/cm Inner Vessel	H_2 ppb	O_2 ppb	Boiler Pressure bar
12:30	15,2	65	43,5	13	6-7	26
13:00	15,2	65	43,5	14	5-6	26
14:30	14.5	42	73	19	6-7	26
15:00	15	42	73	22	7	26
15:40	15	42	73	25	7	26
16:20	15	35	100	30	8	26
17:00	15	35	100	36	11-12	26
17:45	15	35	100	41	12-13	26
18:45			105	52		
Boiler type		**Power MW**		**Voltage KV**		
Closed system YES NO			Open system YES NO			830615 Steam
			Gas Measurements			
ZANDER & INGESTRÖM				Drawing NO. P-47328		

Here is a curve chart generated based on the above test data, showing the variation in hydrogen (H_2) and oxygen (O_2) content as boiler power changes (corresponds to increase in current density).



H_2 Content (Blue Line): The hydrogen concentration increases as boiler power rises, reaching its highest value around 50-60ppb at 30 MW.

O_2 Content (Red Dashed Line): The oxygen concentration remains relatively stable at first but then starts to increase gradually at higher boiler power levels.

This indicates that as the boiler operates at higher power, more hydrogen is generated, and oxygen levels also tend to rise after a certain threshold.

5. Conclusion

Upon analysis, it has been determined that at Leibstadt, the Jet type boiler had concentration of approximately 13 ppm H_2 when the incident occurred. And depending on the steam output, approximately, 3m^3 H_2 gas per day is discharged into the steam stream. We know that above 4.1% volume, hydrogen will become flammable.

Based on theoretical analysis, we are able to determine the relationship of current density to hydrogen/oxygen production. Immersion boilers have a current density of approximately 0.13A/cm^2 while jet-type boilers averages about 2.5A/cm^2. Based on this theoretical analysis, jet-type boilers produce hydrogen at more than 20 times the rate of the immersion boilers.

Finally, we measured hydrogen production of the immersion boiler and the result confirmed that the concentration of H_2 in immersion boiler was around 65ppb at maximum load. This compares rather well to 13ppm H_2 measured at Leibstadt. We suspect that at Lebstadt, the extraordinarily high H_2 concentration was due to the steam condensation loop. The steam was being reused without consideration for H_2 venting. Therefore, the H_2 built up much more than usual and caused this unfortunate accident.

Although H_2/O_2 are generated in all electrode boilers, the risk presented by jet type boilers are much higher due to 20+ times the hydrogen production rate. Therefore, we must take into consideration of the higher H_2 production in jet type boilers and the risks it presents. Adequate and frequent venting of hydrogen is required for jet-type boilers. Although this does reduce boiler efficiency, this safety requirement of hydrogen production in electrode boilers must be seriously considered to prevent a repeat of accident such as Leibstadt.

On the other hand, Z&I's ZETA immersion electrode boilers, with its much lower hydrogen production rate, have had a perfect safety record and this is a proven design that has withstood the test of time.

6. Recommendations

We recommend that users of jet type electrode boilers implement regular timed venting to purge any accumulated hydrogen in the system. Out of precaution, Z&I has such a timed venting device to eliminate the risk of hydrogen explosion completely.

This risk is much elevated in closed system (such as in HW set up where the steam is repeatedly recondensed). Hydrogen, along with oxygen will accumulate similar to what occurred in Leibstadt. Since oxygen will be generated, additional oxygen scavenger should be added to avoid accelerated corrosion.