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Evaluation of inorganic arsenic exposure at multi metal processing facility. When air monitoring alone just doesn't work!

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Abstract

Metals smelting and processing has been associated with exposure to airborne inorganic arsenic and an increased risk of health effects. Biological monitoring on a metals processing site identified urinary arsenic concentrations exceeding corporate and ACGIH guidelines at levels associated with increased risks of health effects. Plant operators considered the inhalation of arsenic trioxide powder (As2O3), used in the process, as the source of their exposure. This study's initial objective was to determine operator exposures to airborne inorganic arsenic. Two groups of plant operators participated in full shift personal air monitoring and biological monitoring over their working weeks. In parallel, wipe samples were taken from control rooms and grab sampling for arsine was carried out to capture a wider range of potential exposure routes. Air monitoring results did not approach exposure standards, with many below the limit of detection. In contrast, biological monitoring results exceeded corporate and the ACGIH guidelines indicating exposure via routes other than inhalation. This demonstrates that relying on air monitoring alone for exposure assessment is inadequate. The findings informed management and workers of practical measures required to adequately control process emissions, secondary exposure due to contaminated surfaces, and poor personal hygiene, prior to the closure of the plant and cessation of all associated processes in early 2015. Assessment of occupational exposure to substances with multiple exposure routes should not rely on air monitoring alone; but integrate other evaluative techniques such as biological monitoring (where available) to ensure exposure risk via all routes is adequately evaluated.

Keywords

processing, facility., arsenic, when, exposure, air, monitoring, just, multi, doesn't, work!, evaluation, metal, inorganic, alone

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EVALUATION OF INORGANIC ARSENIC EXPOSURE AT MULTI METAL PROCESSING FACILITY

WHEN AIR MONITORING ALONE JUST DOESN'T WORK!

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ABSTRACT

Metals smelting and processing has been associated with exposure to airborne inorganic arsenic and an increased risk of health effects. Biological monitoring on a metals processing site identified urinary arsenic concentrations exceeding corporate and ACGIH guidelines at levels associated with increased risks of health effects. Plant operators considered the inhalation of arsenic trioxide powder (As_2O_3), used in the process, as the source of their exposure.

This study's initial objective was to determine operator exposures to airborne inorganic arsenic. Two groups of plant operators participated in full shift personal air monitoring and biological monitoring over their working weeks. In parallel, wipe samples were taken from control rooms and grab sampling for arsine was carried out to capture a wider range of potential exposure routes.

Air monitoring results did not approach exposure standards, with many below the limit of detection. In contrast, biological monitoring results exceeded corporate and the ACGIH guidelines indicating exposure via routes other than inhalation. This demonstrates that relying on air monitoring alone for exposure assessment is inadequate.

The findings informed management and workers of practical measures required to adequately control process emissions, secondary exposure due to contaminated surfaces, and poor personal hygiene, prior to the closure of the plant and cessation of all associated processes in early 2015.

Assessment of occupational exposure to substances with multiple exposure routes should not rely on air monitoring alone; but integrate other evaluative techniques such as biological monitoring (where available) to ensure exposure risk via all routes is adequately evaluated.

INTRODUCTION

Concerns had been raised by a work group about exposure to airborne inorganic arsenic (As) during the treatment of slurry to remove impurities enabling the recovery of zinc through electrowinning. During the purification process a fine arsenic trioxide (As_2O_3) powder was manually added to treatment tanks. A review of biological monitoring data found the urinary As concentrations of plant operators in all roles varied considerably but had on occasion exceeded corporate standards and the American Conference of Governmental Industrial Hygienists (ACGIH) biological exposure indices (BEI). Plant operators were adamant that exposure to the As_2O_3 powder was responsible for their elevated urinary As results, and that this had only become a problem since they switched from a granular to powder form of As_2O_3.

Air monitoring for As in the plant had previously been carried out, however current exposures, the routes of entry associated with elevated urinary inorganic arsenic, or the reason for the large variability in these results remained undefined.

An initial appraisal was carried out comprising a preliminary walk through survey on 18th March 2014. This was followed by full shift personal air and daily biological monitoring of 2 individual plant operating teams, over separate working weeks 24th - 27th March and 3rd - 6th April 2014. In addition, surface wipe samples were collected from a number of operator contact surfaces. Further assessment was carried out on 16 April 2014 when grab sampling for arsine was undertaken.

The purpose of the assessment was to;

- Assess the effectiveness of current control measures
- Determine operator exposures to airborne As

- Evaluate compliance to regulatory duties under the South Australian WHS Regulations 2012 relating to the management of risk and workplace exposure standards
- Identify sources of As exposure, and
- Determine the potential risk of adverse health effects for plant operators.

A literature review was carried out using data bases including Scopus; Pub Med and Web of Science. Search terms included, arsenic exposure, arsenic trioxide, smelting, zinc leaching, hydro metallurgy. There is an extensive body of literature on the toxicology of As and known health effects particularly relating to environmental exposure via contaminated drinking water. By comparison there is a relatively small body of information and limited epidemiological studies on occupational exposure to As and associated risks to health *(Lubin JH, 2000).*

There are limited numbers of studies on occupational exposure via ingestion or skin absorption with most focused on exposure via inhalation and the association with lung cancer *(IARC, 100C)*. There was an absence of information regarding As exposure associated with hydro-metallurgical zinc purification; addition of As_2O_3 during metal refining or processing; or the removal of filtration residues.

Inorganic Arsenic is classified is a group 1A carcinogen via all routes of exposure *(IARC, 100C)*, with acute health effects including, diarrhoea, vomiting and damage to the peripheral nervous system. Chronic effects can range from cerebrovascular and cardiovascular disease to skin disorders and cancer *(Ratnaike, RN, 2003)*. The risk of adverse health effects associated with arsenic exposure follows a dose response relationship with Lubin JH, 2008 finding the dose intensity to be a major influencing factor.

The principal routes of occupational exposure for inorganic As are inhalation and ingestion with Inhalation considered the principal route *(IARC, 100C)*. While As can enter via the skin, absorption via this route not typically considered significant *(Lundström NG, 2007),* with the exception of As in solution and organic forms used in pesticides *(Wenzel R, 2001, ACGIH, 2001b).*

The Australian exposure standard for As and inorganic compounds is 50µg/m^3 *(HSIS, 2016)*. This is significantly higher than the voluntary standard the company has implemented of 10µg/m^3, which is equivalent to the US Occupational Safety and Health Administration Standard *(OSHA, 1910)* and health based Threshold Limit Value listed by the ACGIH *(ACGIH 2016).*

The collection of urine samples and analysis for inorganic As and its metabolites is the recommended biological monitoring method for assessing exposure to As via all routes *(ACGIH, 2001b)*. The Australian regulatory authority SafeWork Australia has not set a biological exposure limit for As, though SWA, 2013a advises urinary total concentrations of inorganic As and its metabolites > 35µg/L are indicative of occupational exposure and should be investigated. This aligns with the value adopted by the company and BEI given by ACGIH,2016 of 35µgAs/L relating to exposure via inhalation at the 10µg/m3 TLV.

PROCESS DESCRIPTION

The zinc leach plant was a large open plan workspace within an enclosed structure. The plant housed a series of sequential operations where a process known as cementation was used to remove impurities such as antimony; cobalt and cadmium from a zinc rich slurry, resulting in a " Purified" liquor suitable for the recovery of zinc through electrowinning in an adjacent plant.

A continual batching process operated through 2 identical parallel systems, with 5 batches purified on a typical working shift. Slurry entered the east end of the plant moving through the system, maintained around 85^{o}C until the final product exited the plant for storage in a large open tank.

The multi stage process commenced with iron purification in initial leach tanks where electrolytic acid and iron were added to separate coarse solids and some impurities from a slurry. The treated solution was then pumped through a series of burt filters which extracted the available solids with the filtered liquor passing through into a staging tank.

The liquor then entered 1st stage purification tanks where additional acid, copper sulphate, zinc dust and As_2O_3 were added initiating a cementation reaction whereby most impurities dropped out of the solution forming a solid.

When the 1st stage purification was completed the solution passed through a filter press located to the west of the purification tanks, separating the solids from the liquor which passed through to 2nd stage purification tanks to continue further cementation. After allowing further time from cementation the solution was is passed through another finer filter press exiting the process into external holding tanks ready for electrowinning.

The plant operated continuously, manned by 4 operators working 12 hour shifts with a 1 hour break over a 48 hour weekly roster. Shift blocks consisted of 2 days 5.30am-5.30pm followed by 2 nights 5.30pm-5.30am and 4 days off, though occasional overtime could be worked on rostered days off. Tasks carried out in the plant primarily occurred on the first floor level aligned with the top of the tanks.

Operators were permanently assigned one of 4 primary roles known as Initial Leach; Burt filtration; Purification and Filter press/water treatment. While operators moved throughout the workspace each role was associated with a particular stage in the overall process and localised area where the majority of the operators tasks were performed.

The purification operator was the only team member in direct contact with As_2O_3, handling or adding it into the process during typical production, occasionally the filtration/water treatment operator occasionally performed this function when acting as relief.

The purification operator carried out the following tasks where potential contact with As_2O_3 or process solution was observed; Collection and deposit of As_2O_3 Billie cans from storage; adding As_2O_3 into stage 1 purification tanks; sampling and analysis of tank liquor in particular for pH levels; adding zinc dust, copper sulphate and spent to systems; data entry and monitoring of system information in purification control; general cleaning of the area.

All 4 purification tanks had level sensing systems in place and extraction systems built into the lids, configured as 2 independent fans and ducts of the same diameter, with one travelling in a straight line before changing direction vertically to form an exhaust stack.

The second duct joining the first at an angle with no change in the diameter of the now merged duct (Image 1).

The capture face of the ducts penetrated well below the height of the lids into the tanks.

Image 1: Purification tank extraction system *(Roseberg 2015*

Despite the extraction system in place, emissions from the tanks were frequently observed with operators commenting this was exacerbated by high solution levels.

Purification tank samples were continually tested throughout each batch with a heavy focus on pH levels particularly prior to As_2O_3 addition. Examination of a plant risk assessment from2014 found the combination of zinc, and As_2O_3 results in a risk of arsine generation if the solution is allowed to drop below 3.4 pH. Operators did not typically wear gloves during the collection or analysis of samples.

Plant procedures required the 2 kg of As_2O_3 in the billy to be added from the via a raised chute in the purification tank lids the chute was located adjacent to hole in the lid where samples were collected using a long handled dip stick. The billies of As_2O_3 powder were transported and stored in a trolley cart adjacent to the stage 1A tank fill point (Image2). As_2O_3 addition took less than 2 minutes occurring at the start of each batch, then at 25 and 60 minutes intervals.

When adding As_2O_3 (Image 3) operators wore a disposable single use P2 half face respirator (3M model 9926) and (Excalibur W6300R) chemical gloves; one operator wore (Uvex Profi-Ergo ENB 20A) gloves.

Both gloves and disposable respirators were re-used for the entire shift and occasionally more than one.
A Drager Pac III arsine gas monitor (PAC-III) Serial No ERXE-0137 calibrated 03/12/2013 was worn intermittently, at other times it was left inside an adjacent sample room as operators complained SO_2 emissions from nearby processes caused it to alarm.

Image 2: As_2O_3 trolley, chute and sample opening *(Roseberg 2014)*

Image 3: Addition of As_2O_3 *(Roseberg 2014)*

Operators carried out data entry and system monitoring in the purification control room where breaks were also taken; most contact surfaces and equipment in the room were heavily soiled. There was an airlock in place but the external door was damaged and remained open.

METHODS AND MEASUREMENT

An initial appraisal was carried out comprising a preliminary walk through survey on 18th March 2014, followed by full shift personal air and daily biological monitoring of 2 individual plant operating teams over separate working weeks 24th - 27th March and 3rd - 6th April 2014. Surface wipe samples were also collected from a number of operator contact surfaces. Further assessment was carried out on 16 April 2014 when grab sampling for arsine was undertaken.

Personal air monitoring was carried out to collect the inhalable dust fraction in accordance with *(AS 3640:2009)*. Operators were fitted with SKC Airchek Universal Sampling pumps model 224-PCXR4, drawing air through Institute of Occupational Medicine (IOM) samplers located in the breathing zone. Samplers were fitted with 0.8µm x25mm SKC Cellulose Ester Membrane filters (Lot, 13178-7DD-028 Expiry Date 2/2018)with a field blank accompanying each batch as discussed by Cherrie J, 2010; p40.

Flow rates were set to 2 L/m for each sampling train, on commencement and verified at the completion of monitoring using a Dwyer Veriflow rotameter, model VFB-65-SSY-10B Identification Number NPP-4, calibrated against a primary bubble flow meter 03/03/2014. All flow rates were found to have deviations of <10% resulting in no samples being discarded.

Analysis of personal air monitoring samples was carried out by the onsite NATA accredited laboratory to (NIOSH method 7300) using inductively coupled argon plasma (ICP), atomic emission spectroscopy (AES). All analytical results were downloaded to an excel spread sheet from the sites internal data management system.

A unique sample numbering system incorporated the 4 digit laboratory analytical process number (3072), followed by the sampler/badge number (5) and the date relating to when sampling commenced 23/03/2014 (23314) written as 3072-5-23314. Filters used for personal monitoring were not weighed before or after sampling as a microbalance with the necessary accuracy was not available. This prevented determination of metals as a percentage of total dust.

To account for all potential exposure routes all operators participating personal air monitoring also underwent biological monitoring for As in urine. Operators provided a sample at the commencement of the working week to establish a base line, and at the completion of each shift. Due to cost constraints sampling at the start of each shift could not be included in the biological monitoring strategy. Analysis of urine samples via solvent extraction and ICP-MS was carried out by an external NATA accredited provider speciated to provide the results as the sum of inorganic As and its metabolites following the guidance of SWA,2013a.

To assist evaluating current the site biological monitoring program and ensure sample contamination was minimised, a trial method was implemented for the collection and handling of urine samples following the guidance of *(AS 4985:2002)*.

To assess contamination of control room surfaces wipe samples were taken on 26/03/2014 with one field blank accompanying the samples for analysis. Wipe tests were carried out using Environmental Express 150 x 150mm Ghost Wipes™ Metal Testing Wipes (Batch# 4210). Areas of 300x300mm^2 were sampled following the guidance of Appendix 13.1

Guidelines for the Evaluation and Control of Lead Based Paint Hazards in Housing *(US HUD, 2012)* with analysis carried out by the onsite Laboratory following a NATA accredited in house method 653-00045 for metals via ICP-AES.

The four primary roles in the plant, their locations and potential exposures were distinct from each other. As a result no operator roles could be combined to form a SEG. However the activities and potential exposures of the operational roles were consistent both daily and across the 4 shifts, therefore operators across the 2 shifts performing the same role were considered SEGs during the analysis and evaluation of results.

Statistical analysis of personal air monitoring and biological monitoring results was carried out using IHSTAT + V, 235 *(AIHA, 2013)*. Following the method explained by *(Hewett P, 2007)* results below the analytical limit of detection (LOD) given by the laboratory as 0.2µg, were divided by half and entered as 0.1µg.

The Australian exposure standard for As and its compounds is an 8hr TWA of 50µg/m^3 *(HSIS, 2015).* The company adopted a more conservative corporate exposure standard of 10µg/m^3. Using the IRSST utility for the adjustment of TWA *(IRSST, 2015a)* discussed by *(AIOH, 2013)* a correction factor of 0.8 was applied for the 12 hour shift being worked, resulting an adjusted regulatory standard of 41µgAs/m^3 and corporate standard of 8µgAs/m^3

The company implemented an action/ investigation level of 20µgAs/gCr and a removal level of 35µgAs/gCr, above which the operator should be removed from As risk work. As recommended by *(ACGIH 2016; p109-111)* these levels were not adjusted for extended working hours.

RESULTS AND DISCUSSION

Monitoring and sampling comprised 32 personal air-monitoring samples with 8 controls; 36 urine samples (8 pre and 28 post shift) and 4 surface wipe samples including 1 control. Subsequent grab sampling for arsine included 6 measurements 3 with a direct reading instrument and 3 using colorimetric indicator tubes.

Personal Air Monitoring

Personal air monitoring results were calculated following *(AS3640, 2009; p15)* and summarised by assigned operator number for teams 1 and 2 in tables 1 and 2 respectively. Due to the more conservative nature, comparison of personal air monitoring results was carried out against the adjusted corporate standard. Protection factors for respiratory protective equipment were not taken into consideration as its use was not commonplace within the plant.

Table 1: Team 1 Personal Monitoring Results in µgAs/m^3

Operator No	Results 24/03/14	Results 25/03/14	Results 26/03/14	Results 27/03/14
1	<0.2	0.25	<0.2	<0.2
2	0.65	<0.2	0.22	<0.2
3	0.53	0.47	0.76	0.59
4	<0.2	0.78	<0.2	<0.2

Table 2: Team 2 Personal Monitoring Results in µgAs/m^3

Operator No	Results 03/04/14	Results 04/04/14	Results 05/04/14	Results 06/04/14
5	0.35	<0.2	0.56	<0.2
6	<0.2	<0.2	<0.2	Absent
7	3.03	0.99	0.31	0.61
8	Absent	<0.2	<0.2	<0.2
9	<0.2			
10				2.36

These results should be viewed with consideration to a number of observations. On 25/03/14 operator 4 spent an extended period cleaning up a filter press 1 residue spill while not wearing an apron or gloves. The operator also spent time assisting in purification. Maintenance carried out a test of the purification control pressurising unit without warning on 03/04/14. This caused a significant amount of accumulated dust to be blown around the room where operator 7 was working.

Team 1 production was reduced to 3 batches per shift with individual As_2O_3 additions of 6kg during across the sampling period. Team 2 operated under full production of 5 batches per day and increased As_2O_3 additions to 8kg. A large amount

of steam was frequently observed being emitted from the As_2O_3 addition chute (Image 4). The operators were observed adding As_2O_3 through the adjacent sampling grate (Image 5) and cited concerns that the escaping steam could result in the As_2O_3 being blown back out of the chute as the reason.

Image 4: Steam rising from chute *(Roseberg, 2014)*

Image 5: Grate used to add arsenic *(Roseberg, 2014)*

The cumulative results for team 2 were higher than those of Team 1 however included 1 significant high outlier. With the exception of the purification operator SEG, air monitoring statistics (tables 3 and 4) did not pass the W-test applied by the IH-Stat tool. Failing to fit either a normal or log-normal distribution the statistics derived are observational only. The arithmetic mean was used to examine the data due to this lack of distributional fir, in addition to being a more appropriate measure for substances associated with acute health risks compared to the GM which may underestimate exposures. Note; for statistical analysis results below LOD entered as 0.1

Table 3: Team 1 Personal Monitoring Results in µgAs/m^3

Operator No	No Samples	Min	Max	Range	Arithmetic Mean
1	4	<0.2	0.25	0.15	0.14
2	4	<0.2	0.65	0.55	0.27
3	4	0.47	0.76	0.29	0.59
4	4	<0.2	0.78	0.68	0.27

Table 4: Team 2 Personal Monitoring Results in µgAs/m^3

Operator No	No Samples	Min	Max	Range	Arithmetic Mean
5	4	<0.2	0.56	0.46	0.28
6	3	<0.2	<0.2	0	0.1
7	4	0.31	3.03	2.72	0.31
8	3	<0.2	<0.2	0	0.1
9	1	<0.2	<0.2	NA	NA
10	1	2.36	2.36	NA	NA

The purification operators had the highest exposure profile within the plant both individually and as a SEG though this was still less than 15% of the adjusted corporate standard. The statistics for this SEG (table 5) formed a log normal distribution with a geometric mean > 3 times that of any other SEG or team statistic, despite being more conservative then the arithmetic mean used for those groups.

Table 5: Purification operator statistics in µgAs/m^3

No Samples	Range	GM	GSD	95th percentile	UCL	UTL
8	2.71	0.85	2.20	3.09	2.74	10.4

Wipe Samples;

Wipe samples were taken on 26/03/14 of contact surfaces in the control rooms with results detailed in table 6. Lead is a common accumulating contaminant on site and a good measure of hygiene practices, so its presence was also assessed.

Table 6: Surface Sample Locations and Results in µg

Date	Sample	Location	As	Pb
26/03/2014	3072-20-26314	Control	0.38	14.4
26/03/2014	3072-21-26314	Control room CPU desk	27.6	1305.2
26/03/2014	3072-22-26314	Control room dining table	5.6	172.1
26/03/2014	3072-23-26314	Purification CPU desk	21.3	135.5

There are no Australia regulatory standards relating to surface contamination of a workplace by As or lead. The results in table 11, show elevated levels of both As and lead on all surfaces tested, with lead concentrations exceeding the site standard of 100µg/300mm^2.

Biological Monitoring

There were no samples rejected with all observed creatinine concentrations within the World Health Organisation guidelines of > 0.3 g/l and <3.0 g/l *(ACGIH, 2016, pg109).* Samples were not provided by team 1 operators 1 and 3 on Thursday 27-3-2014 or operator 4 on Friday 28/3/2014. Overall the compliance rate for biological monitoring was 90% during the trial which was sufficient for a representative data set.

Repeating the pattern seen in personal air monitoring the biological monitoring results for team 2 were statistically higher than those of team 1 for all groups; in particular the end of week sample. Figure 1 highlights the variation between the 2 teams in addition to the progressive increase in urinary concentration from the baseline over the working week.

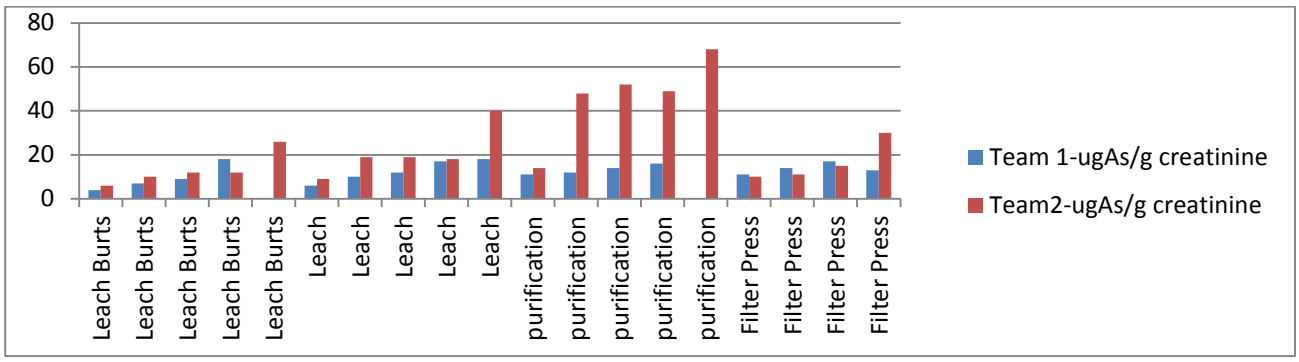

Figure 1: comparison of team biological monitoring results

The consolidated biological monitoring results for both team 1 and 2 formed a log normal distribution. Comparison of the of the teams GM for urinary As (table 7) further demonstrated the significantly higher end of week urinary As concentration of team 2 compared to team 1. The end of week urinary As GM were significantly higher than the baseline GM for both teams, with increases over the working week compared to the baselines in the teams GM urinary arsenic of 180% and 254 % for teams 1 and 2 respectively.

Table 7: Surface Sample Locations and Results in µg

Name	No of samples	GM - Pre shift baseline sample	GM - End of week sample	% change in GM over week compared to baseline
Team 1	17	7.3	13.1	180%
Team 2	19	9.3	23.6	254%

With one exception figures 2 and 3 show creatinine corrected urinary As levels consistently increased as the week progressed from the pre shift baseline for both team 1 and 2 respectively. The results also highlight the potential fluctuations in urinary As concentrations over the working week, reflecting both the reasonably short biological half-life and variability in exposure. The urinary As results of operators on their first day back from a standard roster break, did not

significantly exceed the background levels expected from non-occupationally exposed populations between 8-10µg/gCr *(WHO, 2000)*. This indicates the consistent increase in urinary As observed across the working week reflects occupational exposure.

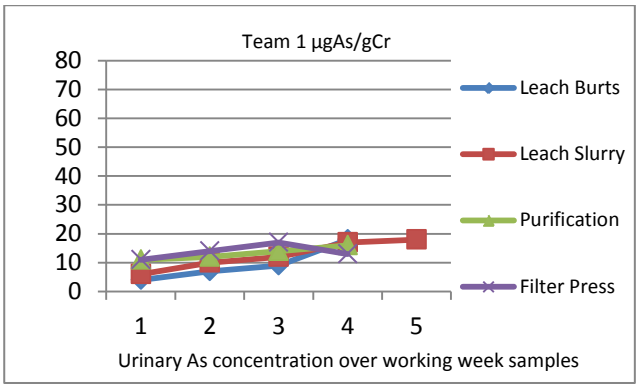

Figure 2: Team 1 biological monitoring results from baseline

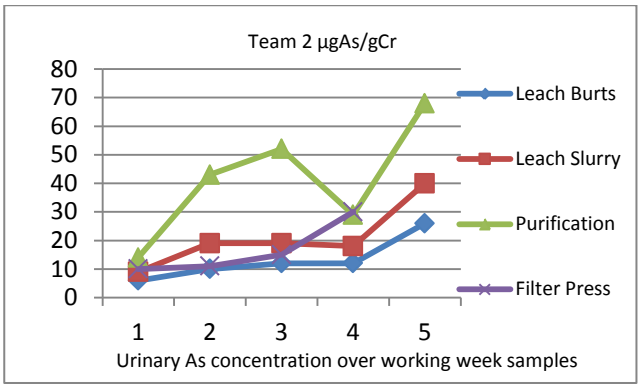

Figure 3: Team 2 progressive sample results from baseline

A number of creatinine corrected results particularly from team 2 exceeded the corporate action 20µg/gCr and removal levels 35µg/gCr. Additionally a number of uncorrected results exceeded the ACGIH BEI of 35µgAs/L. The ACGIH BEI 35µgAs/L is representative of exposure to airborne As at the TLV of 10µg/m3 *(ACGIH 2016: p13&107-111).* As no personal air monitoring results for inorganic As exceeded 30% of the TLV, the urinary As results observed indicated exposure to inorganic As is occurring via the skin; ingestion; or to another form of As such as arsine.

Consistent with the personal air monitoring results, biological monitoring statistics for the purification SEG significantly exceeded those of the other groups. The group results for team 2 were again higher than team 1 for all statistical measures.

With the exception of production volume there were no significant differences in the activities of the teams or tasks carried out. Urinary As concentrations typically increased across the work week with team 2 returning significantly higher overall results. This indicates exposure to As in the plant is directly related to and influenced by production levels/ batch numbers, and regular activities.

The purification operator statistics indicated a high probability of creatinine corrected urinary arsenic concentrations exceeding the corporate removal level. Statistics summarising post shift urinary results indicate a potential for all SEGs to return creatinine corrected urinary arsenic concentrations exceeding the removal level.

Sampling For Arsine

When investigating alternative sources of As exposure the potential for an unidentified exposure to arsine became apparent. Arsine is metabolised and eliminated almost identically to As *(NOHSC, 1989)*, resulting in the same metabolites with a longer half-life *(Yoshimura Y, 2011).*

Exposure to 0.005ppm arsine is associated with urinary As concentration of approximately 48µgAs/L *(ACGIH, 2007).* The Australian regulatory and corporate exposure standard for arsine is 0.05ppm *(HSIS, 2016a)*. STEL or BEI are not recommended for arsine due to its acute toxicity *(ACGIH, 2007)*. The adjusted exposure standard for a 12 hour work shift calculated using the IRSST utility, was 0.03ppm.

Grab sampling for the assessment of arsine was carried out on 16/04/2014 in the area surrounding the stage 1 purification tanks detailed in table 8. This was where As_2O_3 addition occurred therefore where arsine was most likely to be found. Three measurements were taken using the plants PAC-III, fitted with an arsenic hydride sensor, Serial No ERXE-0137 calibrated 03/12/2013. The PAC-III also has positive cross sensitivity to Sulphur Dioxide SO_2 *(Drager, 2015)* which can enter the plant from adjacent processes.

To control for this interference three concurrent samples were taken, using CH25001 Drager colorimetric Indicator tubes; batch FF-0581; expiry date August 2015 which are unaffected by this cross sensitivity. Air was drawn through the tube using

a Drager 100 millilitre gas detector pump, model 31 Serial No 000596/89, compressed 20 times for a volume of 2L per sample giving a detection range of 0.05 - 3ppm *(Drager 2011).*

Table 8: Grab Sampling Locations and Results in PPM

Date and Time	Time mins	Location	Result PAC III ppm	Result -increment range shown on indicator Tube ppm
16/04/2014 - 14:20	2	North western side stage 1 purification tank A	0.08	>0.05 - <0.25
16/04/2014 - 14:25	2	South side stage 1 purification tanks A	0.02	<0.05
16/04/2014 - 14:30	2	Upper platform stage 1 purification tank A	0.08	>0.05 - <0.25

While these measurements represent only a single assessment and time period, the results confirmed there was a potential for arsine to be present at concentrations equal to or exceeding the corrected exposure standard. Unprotected exposure to the concentrations identified had the capacity to result in urinary As concentrations well in excess of the corporate standards.

When questioned, most operators reported they are familiar with and often smell the garlic odour of arsine; particularly after As_2O_3 addition. Arsine has an odour threshold of 0.5ppm *(ASTDR, 2015)* 10 times the PAC-III alarm level set at the regulatory exposure standard of 0.05ppm. the odour threshold is well above the concentrations between 1 - 3 ppm where prolonged exposure is associated with adverse acute health effects *(ACGIH, 2007).*

CONCLUSIONS

Despite operator concerns and observable potential exposure to airborne As, personal exposures did not exceed the corporate exposure standard of 8µgAs/m^3, and were well below the regulatory exposure standard of 50µg/m^3. While statistics for the purification SEG indicate a slight potential exposures to airborne As in the vicinity of 10µg/m^3, operator exposures determined were not at concentrations typically associated with acute health effects or those associated with an increased risk of chronic health effects. The purification SEG results may have represented the culmination of very short high intensity exposures during As_2O_3 addition <2minutes which may require further investigation.

The report findings identified practices resulting in direct skin contact with process solutions and contamination of control rooms and internal surfaces by As and Pb. Poor personal hygiene practices were also observed by plant operators who were at risk of secondary exposures via ingestion in addition to a lesser but still potentially relevant exposure via dermal absorption.

Despite the implementation of considerable control measures to minimise the potential for the generation of arsine and reduce exposure, the sampling results indicated plant operators were at risk of exposure to arsine at concentrations potentially exceeding corporate and regulatory exposure standards.

Contrasting the findings of personal air monitoring; biological monitoring results exceed the site action, removal levels and the ACGIH BEI guidance value of 35µgAs/L. Biological monitoring results indicated a reasonably likelihood that under normal operating conditions these values may be significantly exceeded, particularly by the purification SEG with a UCL of 66.8µgAs/gCr. Urinary As concentrations of plant operators exceeding these values for any extended periods may result in an increased risk of chronic adverse health effects *(ATSDR, 2007; ACGIH, 2001a).*

With the exception of production volume there were no significant differences in the activities of the teams or tasks carried out. Urinary As concentrations typically increased across the work week with team 2 returning significantly higher overall results. This indicates exposure to As in the plant is related to and influenced by production levels/ batch numbers, and regular activities.

The trial method for the collection and handling of biological monitoring resulted in a significantly reduced range and variability, compared to past results across the site. This demonstrated the existing site collection practices were not adequately minimising sample contamination

The results of this assessment indicate elevated urinary As observed is a result of plant operators being exposed to As via multiple exposure routes and exposure to arsine also strongly indicated. The capture face of the extraction ducts were found to penetrate into the tank well below the inner surface of the lid which had numerous openings. This allowed a significant vapour space behind the capture zone in the top of the tank. Issues with level indicating equipment resulted in purifications tanks often being overfilled bringing the surface of the solution very close to the capture face of the ducts visibly increasing tank emissions from the lid. Combined with the ineffective use of pH, These matters were likely to be significant factors influencing the risk of arsine generation and any subsequent emission from the purification tanks.

The previous assessment carried out in the plant found no detectable exposures to As but did not incorporate surface sampling or biological monitoring. The results of this appraisal clearly demonstrate current practices using air monitoring alone for exposure assessment are not adequate when evaluating exposure to substances with multiple routes of entry.

RECOMMENDATIONS AND OUTCOMES

Immediate Implementation;

Electronic PH monitoring equipment and automated tank level indicating systems required inspection and reinstatement to working order.

An investigation into granulated or liquid alternatives to the As_2O_3 was undertaken. The use of liquid alternatives was determined to introduce significant hazards and risks to health. No manufacturers were able to provide a granulated alternative in the quantities required. As a result an evaluation of closed chemical transfer systems was initiated.

A full review of all PPE used in the plant was required. At the time of this assessment filters certified for arsine use were not available. At the request of the company, 3M Australia had their ABEK acid gas filter evaluated and verified for protection against arsine. This use of the ABEK in combination with a P2 filter was recommended to be made mandatory for respiratory protective devices worn in areas where there is a risk of arsine exposure and during the handling and addition of As_2O_3. The Uvex Profi-Ergo ENB 20A were recommended to be replaced with PVC gauntlets listed as suitable by the As_2O_3 safety data sheet and meeting the requirements of AS/NZS2161.1:2000.

Plant operators to be provided with refresher training in personal hygiene requirements. Plant hygiene practices were to be reviewed with a thorough clean of all control rooms focusing on internal contact surfaces.

Plant operators with elevated urinary As are to be referred to the site medical practitioner for a medical assessment relating to As exposure and investigation of any symptoms or signs of adverse health effects.

The trial method applied for the collection and processing of urine samples was adopted site wide and incorporated into the site biological monitoring protocol for all substance. A review of the sites biological monitoring program was also required and completed late 2014 ensuring all operators at risk of exposure to As including maintenance personnel were captured.

For all future exposure assessments on site encompassing substances with multiple exposure routes biological monitoring is required where practicable methods and BEIs are available.

Further Considerations;

The purification extraction system required assessment by a ventilation engineer, with particular attention to duct work design and airflow balance between the independent fans following the guidance provided in *(HSG 258; DOE 1989; Reed et, al 2013: p116-123)*

The alarm levels of the PAC-III arsine monitors should be altered from 0.05ppm to 0.03ppm to reflect the exposure standard adjusted for 12 work shifts.

Once corrective measures have been undertaken to address tank emissions and pH control systems, a review of surface contamination and biological monitoring results should be carried out to evaluate the effectiveness of the control measures in place. This review should coincide with a more detailed investigation of operator exposure to arsine due to its potential for acute toxicity following *(NIOSH method 6001)*.

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