A Study of Underground Coal Gasification (UCG) Wastewater and Sludge

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ABSTRACT: Underground coal gasification (UCG) is a non-conventional method of extracting gas from coal. The primary advantage of UCG is that it recovers gas from uneconomical or unminable coal, potentially increasing the value of the world's coal reserves by an estimated 70%; for this reason, UCG has been implemented at sites around the world. However, the gaseous, liquid and solid waste streams which accompany UCG are the source of known mutagens and carcinogens, and potential contamination of groundwater has been identified. In the absence of any meaningful data on UCG waste, this study sought to identify the main organic and inorganic chemical and odoriferous properties of UCG wastewater and sludge from a site in Australia, and examined the roles of oxidization, biostimulation and metal sequestration in the treatment of wastewater and sludge generated by the gasification process. Findings suggest that UCG wastewater and sludge emanate a highly objectionable odour and contain significant concentrations of benzene, toluene, a range of petroleum hydrocarbons, and phenols, but relatively low levels of heavy metals and no polycyclic aromatic hydrocarbons, pesticides or polychlorinated biphenyls. Both oxidation and biostimulation destroyed organic contaminant species by >95%, and sequestration reduced inorganic contaminant species by >94%. As this represents one of the first reliable studies to investigate UCG odour, wastewater and sludge, further research is required to better understand and document the environmental and human health effects, if any, of short-term and chronic exposure to these types of wastes.

Key words: Underground coal gasification, UCG, Wastewater, Sludge, Odour

INTRODUCTION

Despite underground coal gasification (UCG) first being described as a possible way to liberate combustible gas from rock in the late 19th century (Siemens, 1868) and despite it being used extensively throughout the world during the 20th century (Klimenko, 2009; Lamb, 1977), implementation of the process has been torturous. For example, a significant range of industrial accidents and spills have plagued the industry, and attempts to introduce the technology in Australia and the United Kingdom, for example, have met with profound resistance from urban and rural communities and groups (Australian Associated Press, 2011; Roberts, 2014; Yeo, 2013). The names of action groups such as "Frack Off" and "Druids Against Fracking" in the UK and "Lock the Gate Alliance" and "Unite to Fight" in Australia summarize the views of many people toward UCG in these countries.

The most fundamental hurdle UCG has had to overcome is its reputation as a despoiler of the environment, particularly as a benzene and toluene contaminator of groundwater (e.g., Bajkowski, 2014; Sury, *et al.*, 2004; U.S. Environmental Protection Agency, 1999). For this reason, initiatives to better understand, manage and treat the various gaseous, liquid and solid waste streams generated by UCG operations have become a priority for government regulators and industry.

In simple terms, UCG (and its related "coal seam fire") extraction involves: 1) drilling a well into a coal cavity (usually at a depth between 150m and 1500m) which contains gas, often using the so-called "CRIP method" (Burton, *et al.*, 2004); 2) pumping air or oxygen into the well; 3) igniting the air or oxygen to cause high pressure combustion; 4) as a result of this "controlled combuston" at between 900-1500°C, allowing partially combusted gases to rise to the surface through a secondary production well (sometimes the injection well and the production well must be connected by hydraulic fracturing or "fracking" of rock to create a "panel"); 5) separating the gas into various fractions

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in a processing facility; and 6) collecting and storing the gas for later use.

In this fundamental sense, UCG is dissimilar to its rival coal seam gas (CSG), which depressurizes gas from coal seams either by injecting water into the seam, hydraulically fracturing the coal using chemical fracking fluids, or a combination of both water and fracking fluids. While UCG is considered a more costly process than conventional extraction methods, in theory it provides access to gas trapped in coal belts which would be unminable or uneconomical using conventional methods, including CSG. Some estimates have suggested that by accessing this "unminable" coal, UCG has the potential to increase global coal reserves by 600 billion tonnes or 70%, with India planning to access 350 billion tonnes of gas using UCG (World Energy Council, 2013, p. 1.7). Moreover, up to 20 times more gas can be produced by UCG than by CSG

Unlike CSG, which mostly extracts methane (CH₂), the primary gases generated by UCG are carbon monoxide (CO), hydrogen (H) and carbon dioxide (CO₂), together forming what is referred to as "syngas" (or synthetic gas), with lesser quantities of methane and other gaseous hydrocarbons also coming to the surface. Syngas can be used as an energy source for gas-fired power plants, in the manufacture of synthetic petroleum products, or as fuel for internal combustion engines. Like gas generated from CSG extraction, one of the major benefits of syngas as a generator of electricity is that it burns "cleaner" than coal, with about 21% lower greenhouse gas emissions than convention fossil fuels (Shu-qin & Jun-hua, 2002); UCG is thus referred to as a "clean coal technology" (BHP, 2002).

However, in addition to gases rising to the surface in the production well, a significant amount of wastewater and solids (usually categorized as "process water" or "produced water" by the industry), which results from the high-temperature underground combustion of coal and rock, is also mixed in with the gas, and these waste streams must be separated and managed post-extraction (about 3-5% of UCG wastewater is solids, becoming sludge once settled in the wastewater treatment plant). In addition to the obvious problems associated with treating high levels of benzene, toluene, alkanic hydrocarbons and phenols (some of which are known mutagens and carcinogens), one of the major concerns with UCG (and CSG) is the likelihood of leaving behind toxic liquid in underground chambers and voids where in theory it could contaminate groundwater and aquifers, perhaps well into the long-term future.

It has been argued that because the gasification process occurs below the level of hydrostatic pressure, the likelihood of groundwater contamination is negligible, but at 150+m below the surface it is hard to know, let alone control, the complex combustive and chemical reactions, aqueous phase contaminant transport mechanisms and fluid dynamics of groundwater associated with gasification, and much of the chemistry of UCG and its relation to groundwater is either undisclosed or unknown to researchers, regulators and the wider community. Other problems associated with UCG are subsidence of overlying terrain, fugitive emissions contributing to global greenhouse gases, and long-term underground coal fires which are triggered as a result of underground coal combustion, each of which has been well documented (Burton, et al., 2004), but this study is mostly concerned with investigating issues associated with potential surface water contamination (Sury, et al., 2004, pp. 62-65).

The author was unable to find any published research on the volume or chemical properties of, or approaches to treating, UCG wastewater and sludge (for example, the Queensland Independent Scientific Panel on UCG only makes passing reference to process water [p. 25] in the context of environmental risk, but makes no reference to sludge [2013]; where contaminants like arsenic and mercury are referenced, they are in the context of removal from the gaseous stream [Burton, et al., 2004]). The only reference to UCG wastewater came from a consultant's review. which reported the only contaminants of concern during trials in Wyoming were ammonia at 8.7 mg/L, boron at 1.0 mg/L, and sulfate at 1,000 mg/L, and in Spain with ammonia at 542 mg/L, phenols at 288 mg/L, and sulfate at 74 mg/L (Sury, et al., 2004, pp. 24-28).

The purpose of this study was to examine the chemical and odoriferous characteristics of UCG wastewater and sludge, and to assess the impact of standard industrial wastewater and sludge treatment options on UCG waste. The following three research questions motivated the study: 1) What are the chemical properties of UCG wastewater and sludge; 2) What roles do oxidation, biostimulation and metal sequestration play in the destruction of organic and the removal of inorganic contaminants from UCG wastewater; and 3) What roles do oxidation and metal sequestration play in the destruction of organic and the removal of inorganic contaminants in UCG waste sludge?

MATERIAL & METHODS

Approximately 6.0 kg samples of wastewater (sample 1) and waste sludge (sample 2) were collected

from a UCG wastewater treatment plant at a site in the Surat Basin in Queensland, Australia. The wastewater sample was collected from the liquid fraction of the settling tank and the sludge sample was collected from the bottom of the sludge clarifier. Samples were refrigerated and transported to a testing facility on the Gold Coast and subjected to testing within 48 hours of collection; after treatment had been carried out, untreated and treated sub-samples were refrigerated and transported to a certified laboratory in Brisbane, where they were analysed within 24 hours.

The wastewater sample was divided into three x 2.0 kg sub-samples, the first of which was an untreated control (sub-sample 1A) with a foul-smelling, acrid odour. To test what impact a standard oxidizing agent would have on organic species and to test what impact a sequestering agent would have on inorganic species in UCG wastewater, the second sub-sample (1B) was subjected to the following treatment regime: 1) add 3.5 g/L of hydrogen peroxide (H_2O_2) at 50% strength with pH 2.0 to the sub-sample and mix vigorously for 15 minutes; 2) add 2.0 g/L of ViroBind reagent and mix thoroughly; 3) leave mixed sub-sample for 24 hour reaction and settling time; 4) decant liquid fraction; 5) seal sub-sample and transfer to certified laboratory; and 6) analyse sub-sample 1B for the following analytes: pH, electrical conductivity (EC), odour, benzene ($C_{\alpha}H_{\alpha}$), toluene ($C_{7}H_{\alpha}$), ethylbenzene ($C_{\alpha}H_{10}$), xylene ($C_{e}H_{1}[CH_{2}]_{2}$), total petroleum hydrocarbons (TPH), polycyclic aromatic hydrocarbons (PAH), total pesticides (including dieldrin [C₁₂H₈OCl₆], endrin [C₁₂H₈Cl₆O], and DDT [C₁₄H₉Cl₁₅]), polychlorinated biphenyls (PCBs), total arsenic, cadmium, chromium, copper, lead, nickel and zinc, and total phenols.

To test what impact a standard biostimulation additive would have on organic species and to test what impact a sequestering agent would have on inorganic species in UCG wastewater, the third subsample (1C) was subjected to the following treatment regime: 1) add 10 mL/L of ViroBac reagent to the subsample and mix vigorously for 15 minutes; 2) add 2.0 g/ L of ViroBind reagent and mix thoroughly; 3) leave mixed sub-sample for 24 hour reaction and settling time; 4) decant liquid fraction; 5) seal sub-sample and transfer to certified laboratory; and 6) analyse subsample 1C for the above analytes.

Liquid hydrogen peroxide was used in this study because it is one of the most powerful oxidisers available to environmental scientists (Interstate Technology & Regulatory Council, 2005, pp. 10-12), stronger even than the more common potassium permanganate (KMnO₄), and because Sury *et al.* reported its use in a UCG wastewater trial in Sain (2004, pp. 26-28). In the present slightly acidic wastewater solution, hydrogen peroxide would cause the following oxidizing reaction: $2Fe^{2+} + H_2O_2 + 2H + \rightarrow 2Fe^{3+} + 2H_2O_2$ or the more rapid exothermic Fenton's reaction: $Fe^{2+} + H_2O_2 \rightarrow 2Fe^{3+} + OH + OH$. It should be noted that some chemical compounds present in UCG waste, including phenols, are incompatible with hydrogen peroxide and most oxidants, and sudden reactions may cause fires or explosions (U.S. Department of Health and Human Services, 1978, p. 2).

ViroBind reagent, a powdered chemical formulation with a pH of 9.0 derived from modified alumina refinery residue, has been used to neutralize acid and sequester heavy metals in industrial wastewater and solids (Fergusson, 2004, 2009). Unlike the simple ionic binding of cations through changes in pH and adsorption normally associated with immobilizing chemicals such as calcium hydroxide (CaOH) and sodium hydroxide (NaOH), the metals sequestered in ViroBind become more tightly bound as time passes. This phenomena is due to the fact that ViroBind is composed of a complex cocktail of metals and minerals, including hematite (Fe₂O₂), beohmite (Y-AlOOH), gibbsite (Al[OH]₂) and sodalite (Na₄Al₂Si₂O₁₂Cl), anatase (TiO₂), aragonite $(CaCo_2)$, brucite $(Mg[OH]_2)$, diaspore $(\beta-Al_2O_2,H_2O)$, ferrihydrite (Fe₅O₇[OH].4H₂O), gypsum (CaSO₄.2H₂O), hydrocalumite (Ca₂Al[OH]₇.3H₂O), hydrotalcite (Mg₆Al₂CO₃[OH]₁₆.4H₂O), and p-aluminohydrocalcite $(CaAl_{2}[CO_{2}]_{2}[OH]_{4}.3H_{2}O).$

Of significance in these formulae is the presence of hydroxides and oxyhydroxide compounds which contribute to the acid neutralizing capacity of ViroBind reagent, as well as the positively charged iron-, aluminium-, magnesium- and titanium-based molecules, which not only initially adsorb metals but also lead to precipitation and isomorphic substitution reactions; these reactions are largely responsible for the long-term "sequestration" phenomena observed with inorganic species. For explanations of how metal sequestration and oxidation work synergistically in environmental remediation and how related reagents in the treatment of drinking water, industrial wastewater and sludge, and contaminated soil have been characterized, see Akhurst, et al. (2011), Cark, et al. (2009), Genç-Fuhrman, et al. (2004), and Hutson and Attwood (2008).

ViroBac reagent, a liquid biological stimulant composed of inorganic chemicals, nutrients, surfactants, enzymes and petrophilic microbes, has been used to destroy single-bonded, alkanic hydrocarbons such as benzene, chlorinated hydrocarbons such as trichloroethylene and perchlorothylene, and PAHs such as benzo(a)pyrene and naphthalene (Fergusson, 2012). Unlike standard biological treatments, which are longer term processes harnessing the potential for indigenous bacteria to digest organic contaminants (often in conjunction with injected air or oxygen), biostimulation augments indigenous processes and stimulates their digestive properties, particularly through the use of nutrient and enzyme addition.

The sludge sample was divided into three x 2.0 kg sub-samples, the first of which was an untreated control (sub-sample 2A) with an equally foulsmelling, acrid odour. To test what impact a standard oxidizing agent would have on organic species and to test what impact a metal sequestering agent would have on inorganic species in UCG sludge, the second subsample (2B) was subjected to the following treatment regime: 1) add 10% of hydrogen peroxide (H_2O_2) to the sludge and mix vigorously for 15 minutes; 2) add 25 g/L of ViroBind reagent and mix thoroughly; 3) leave mixed sub-sample for 24 hour reaction time; 4) seal sub-sample and transfer to certified laboratory; and 5) analyse for the following analytes: pH, odour, benzene, toluene, ethylbenzene, xylene, TPH, PAH, total pesticides, PCBs, total arsenic, cadmium, chromium, copper, lead, nickel and zinc, and total phenols.

To test what impact a second oxidizing agent would have on organic species and to test what impact a metal sequestering agent would have on inorganic species in UCG sludge, the third sub-sample (2C) was subjected to the following treatment regime: 1) add 10% sodium persulfate (Na₂S₂O₈) at 99% purity with 6.6% oxygen and pH of 6.0 to the sludge and mix vigorously for 15 minutes; 2) add 25 g/L of ViroBind reagent and mix thoroughly; 3) leave mixed subsample for 24 hour reaction time; 4) seal sub-sample and transfer to certified laboratory; and 5) analyse for the above analytes. Sodium persulphate in powdered form is routinely used as *in-situ* chemical oxidation (ISCO) agent in site remediation because it is more stable than hydrogen peroxide, has the highest level of water solubility of all oxidants, and leaves behind the least harmful by-products (Interstate Technology & Regulatory Council, 2005, pp. 7-10). Concentrations of odour in UCG wastewater and sludge were determined by the average of two independent raters on a five-scale rating scale: 0 =no discernible odour; 1 = not unpleasant regardless of odour and tolerable by all; 2 = unpleasant to be around but tolerable by all; 3 = unpleasant to be around but tolerable to most; 4 = highly unpleasant to be around and tolerable to some; and 5 = extremelyoffensive odour, causes nausea in sensitive people, not tolerable to most.

RESULTS & DISCUSSION

Tables 1 and 2 answer research question 1. Table 1 presents data on the chemical and odoriferous properties of untreated UCG wastewater (1A).

The data show UCG wastewater is somewhat acidic at 4.9 (consistent with the presence of high concentrations of phenols) with electrical conductivity at 14 mS/cm; odour was considered extremely offensive with a rating of 5 (possibly due to the presence of concentrations of phenol as hydroxybenzene $[C_{14}H_{12}O_3]$ and other hydrocarbons).

The data show 1A was relatively high in benzene, toluene, ethylbenzene and xylene (BTEX), with benzene at 1,600 μ g/L and toluene at 180 μ g/L (the recommended level of benzene in drinking water is <1.0 μ g/L in Australia and 5.0 μ g/L in the U.S., with an "immediate danger to life" at 500 mg/L; benzene is rarely found in groundwater at levels $>10 \,\mu g/L$). Although heavy metal concentrations were low, at 6.9% total petroleum hydrocarbons were high, particularly in the C10-C14 fraction (in the range of naphthas, petroleum distillates, and kerosines), and total phenols were also high at 5,500 mg/L (in fact the laboratory reported it had to significantly dilute the sample prior to analysis of phenols because the observed levels interfered with instrumentation). Phenols, in this case OH⁻ bonded to aromatic hydrocarbons, were mostly composed of xylene-based 2-, 3- and 4-methylphenols and 2.4dimethylphenol ($C_{a}H_{10}O$). No evidence was found for the presence of PAHs, pesticides, or PCBs.

Table 2 presents data on the chemical and odoriferous properties of untreated UCG waste sludge (2A). The data show UCG sludge had a neutral pH but odour was considered extremely offensive with a rating of 5. Levels of BTEX were elevated in UCG sludge, with benzene at 420 mg/kg, toluene at 370 mg/kg, ethylbenzene at 140 mg/kg, and total xylene at 720 mg/ kg. Excepting arsenic, heavy metal concentrations were low, but total petroleum hydrocarbons were extremely high at 57% of the solid fraction, particularly in the C10-C14 (120,000 mg/kg), C15-C28 (360,000 mg/kg), and C29-C36 (90,000 mg/kg) fractions, and total phenols were also high at 21,000 mg/kg (or 2.1% of the solid fraction), again composed mostly of 2-, 3- and 4methylphenol. No evidence was found for the presence of PAHs, pesticides, or PCBs.

Table 1 answers research question 2. The data show that both treatments 1B and 1C had a salutary effect on UCG wastewater: pH increased from 4.9 to 7.4 and 7.1 respectively; EC decreased from 14 mS/cm to 0.5 mS/cm and 1.4 mS/cm; objectionable odour decreased from a rating of 5 to 2 and 1; total BTEX decreased from 1,848 µg/L to below the detection limit of $<2.0 \mu g/L$; TPH decreased by 100% from 69,106 mg/L to 56 mg/L; total heavy metal concentrations decreased by an average of 98% (excluding Cu, which unaccountably increased, perhaps due to analytical error because none of the additives used in treatments

Pa rame ter	1A	1B	Percent Change Between 1A and 1B	1C	Percent Change Between 1A and 1C
рН	4.9	7.4	<u> </u>	7.1	
EC (mScm)	14	0.5	97 ↓	1.4	90 ↓
Odour	5	2	—	1	—
Benzene (mg/kg)	1,600	${<}1.0^{\dagger}$	100 ↓	${<}1.0^{\dagger}$	100 ↓
Toluene ($\mu g/L$)	180	${<}2.0^{\dagger}$	100 ↓	${<}2.0^{\dagger}$	100 ↓
Ethylbenzene ($\mu g/L$)	10	${<}2.0^{\dagger}$	100 ↓	${<}2.0^{\dagger}$	100 ↓
mlp-Xylene ($\mu g/L$)	25	${<}2.0^{\dagger}$	100 ↓	$<\!\!2.0^{\dagger}$	100 ↓
o-Xylene (μ g/L)	33	${<}2.0^{\dagger}$	100 ↓	${<}2.0^{\dagger}$	100 ↓
TPH C6-C9 (mg/L)	5.8	0.03	100 ↓	${<}0.02^{\dagger}$	100 ↓
TPH C10-C14 (mg/L)	69,000	53	100 ↓	54	100 ↓
TPH C15-C28 (mg/L)	100	2.8	98 ↓	1.3	99 ↓
TPH C29-C36 (mg/L)	0.2	0.1	50 ↓	0.06	70 ↓
TPH (mg/L)	69,106	56	100 ↓	56	100 ↓
PAH(mg/L)	${<}0.1^{\dagger}$	$<\!\!0.1^{\dagger}$	—	${<}0.1^{\dagger}$	—
Total pesticides (mg/L)	$< 0.1^{+}$	$< 0.1^{+}$		${<}0.1^{\dagger}$	—
PCB (mg/L)	${<}0.1^{\dagger}$	$<\!\!0.1^{\dagger}$	—	${<}0.1^{\dagger}$	—
As (mg/L)	0.13	0.004	97 ↓	0.01	93 ↓
Cd (mg/L)	0.05	$<\!\!0.0001^{\dagger}$	100 ↓	$<\!0.0001$ [†]	100 ↓
Cr (mg/L)	0.23	0.01	96 ↓	$<\!0.0001^{+}$	100 ↓
Cu (mg/L)	0.05	0.01	80 ↓	0.2	400 ↑
Hg (mg/L)	$<\!0.01^{+}$	$<\!\!0.01^{\dagger}$		$<\!\!0.01^{\dagger}$	—
Ni (mg/L)	0.05	$<\!\!0.001^{\dagger}$	100 ↓	< 0.004	92 ↓
Pb (mg/L)	0.05	$<\!\!0.001^{\dagger}$	100 ↓	< 0.0001 [†]	100 ↓
Zn (mg/L)	0.05	0.01	80 ↓	0.007	86 ↓
Total Phenols (mg/L)	5,500	79	99 ↓	78	99 ↓
Average percent change of			100 +		100
organic species		—	100 ↓		100 4
Average percent change of inorganic species (minus Cu)	—	—	96 ↓		96 ↓

Table 1. Analytical results before and after UCG wastewater treatment

[†] Below the limit of detection

1B or 1C contained Cu); and total phenols decreased by 99% from 5,500 mg/L to 79 and 78 mg/L.

Table 2 answers research question 3. The data show that treatments 2B and 2C also had a salutary effect on UCG waste sludge: objectionable odour decreased from a rating of 5 to 2 and 1 respectively; total BTEX decreased by 100% and 97% from 1,650 mg/kg to 3.6 mg/kg and 54.6 mg/kg; TPH decreased by 92% and 87% from 574,100 mg/kg to 48,380 mg/kg and 77,370 mg/kg; total arsenic concentrations decreased by 89% from 110 mg/kg to 13 mg/kg and 14 mg/kg; and total phenols decreased by 99% and 98% from 21,000 mg/kg to 215 mg/kg and 459 mg/kg, although pH increased from 7.1 to 11.8 and 11.5.

This study provides hitherto unavailable data on the chemical and odoriferous properties of UCG wastewater and sludge in Australia. The findings indicate UCG wastewater has a highly objectionable odour and contains elevated concentrations of BTEX, TPH and phenols, but is low or devoid of heavy metals, PAH, pesticides and PCBs. Similarly, the study found UCG waste sludge has an equally objectionable odour and contains even higher concentrations of BTEX, TPH and phenols, but is also low or devoid of heavy metals (except arsenic), PAH, pesticides and PCBs. These findings suggest that UCG wastewater and sludge must be carefully stored, handled, treated and disposed to the environment if the long-term health and safety of workers, the public and the environment are to be protected.

The significance of the odour findings in this study should not be underestimated. Odours emanating from gas extraction in Queensland have

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Parameter	2A	2B	Percent Change Between 2a and 2B	2C	Percent Change Between 2A and 2C
pН	7.1	11.8	_	11.5	_
Odour	5	2	—	1	—
Benzene (mg/kg)	420	${<}0.2^{\dagger}$	100↓	6.4	99↓
Toluene (mg/kg)	370	${<}0.5^{\dagger}$	100↓	12	97 ↓
Ethylbenzene (mg/kg)	140	${<}0.5^{\dagger}$	100↓	5.6	96 ↓
mlp-Xylene (mg/kg)	460	2.2	100↓	19.9	96 ↓
o-Xylene (mg/kg)	260	1.4	100↓	10.7	96 ↓
TPH C6-C9 (mg/kg)	4,100	<10	100↓	120	97 ↓
TPH C10-C14 (mg/kg)	120,000	10,600	92 ↓	18,000	99↓
TPH C15-C28 (mg/kg)	360,000	36,100	90 ↓	56,500	85 ↓
TPH C29-C36 (mg/kg)	90,000	1,580	94 ↓	2,850	97↓
TPH (mg/kg)	574,100	48,380	92 ↓	77,370	87 ↓
PAH (mg/kg)	$< 0.1^{+}$	${<}0.1^{\dagger}$	—	${<}0.1^{\dagger}$	—
Total pesticides (mg/kg)	${<}0.1^{\dagger}$	${<}0.1^{\dagger}$	_	${<}0.1^{\dagger}$	_
PCB (mg/kg)	$< 0.1^{+}$	${<}0.1^{\dagger}$	—	${<}0.1^{\dagger}$	—
As (mg/kg)	110	13	89 ↓	14	89 ↓
Cd (mg/kg)	$<\!\!0.5^{\dagger}$	${<}0.5^{\dagger}$	—	$<\!0.5^{\dagger}$	
Cr (mg/kg)	${<}0.5^{\dagger}$	${<}0.5^{\dagger}$	—	${<}0.5^{\dagger}$	—
Cu (mg/kg)	${<}0.5^{\dagger}$	${<}0.5^{\dagger}$	—	$<\!0.5^{\dagger}$	—
Hg (mg/kg)	${<}0.1^{\dagger}$	${<}0.1^{\dagger}$	—	${<}0.1^{\dagger}$	—
Ni (mg/kg)	${<}0.5^{\dagger}$	${<}0.5^{\dagger}$	—	$<\!0.5^{\dagger}$	
Pb (mg/kg)	${<}0.5^{\dagger}$	${<}0.5^{\dagger}$	—	${<}0.5^{\dagger}$	—
Zn (mg/kg)	${<}0.5^{\dagger}$	${<}0.5^{\dagger}$	—	$<\!0.5^{\dagger}$	
Total Phenols (mg/kg)	21,000	215	99 ↓	459	98 ↓
Average percent change of			00 1		05
organic species	_	_	77 ¥		× 25
Average percent change of inorganic species	—	_	94 ↓	—	94 ↓

Table 2. Analytical results before and after UCG waste sludge treatment

[†]Below the limit of detection

been associated with complaints in neighbouring populations, including headaches, nausea, vomiting, nosebleeds, irritation of nose, throat and eyes, rashes and sores, and asthma (Medibank Health Solutions, 2013, p. 1). Whether these symptoms were the direct result of odours emanating from "naturally occurring" compounds, like alkanic hydrocarbons, or from manmade chemical compounds like those used in facking chemicals in the gaseous emissions of UCG remains unclear, but the evidence does suggest odours emanating from gas extraction processes are linked to a variety of health complaints, although no causal (or even correlational) link between UCG odour and human health has yet to be established.

Perhaps equally worrying was the finding that benzene has been found in air samples collected within 1.2 km of a gas extraction well in Queensland (Medibank Health Solutions, 2013, p. 6), but this finding too has not been irrevocably linked to health complaints. However, there is a clear need for further investigation into whether links exist between: 1) odours emanating from UCG operations and 2) toxic substances present in foul-smelling gases and to 3) levels of exposure and 4) to adverse health outcomes for people in the vicinity of gas extraction operations. Reliable data on these relationships are either nonexistent or have been found wanting, and circumstantial evidence remains largely anecdotal. Moreover, according to the limited scientific literature available on this subject, rigorous and in-depth risk assessments associated with gaseous, liquid and solid waste streams from UCG have not been conducted by either industry or governments.

It should be noted that many jurisdictions have not set limits for exposure to phenolic gas, but where developed occupational health and safety guidelines have put the odour threshold for phenol at 0.4 parts per million (ppm), sometimes lower (e.g., New Jersey Department of Health, 2010, p. 1). This threshold is in stark contrast to the 5,550 ppm and 21,000 ppm concentrations discovered in this UCG waste, although the concentrations of airborne phenol and hydroxybenzene were not established by this study.

Moreover, because phenols are mutagenic and possibly carcinogenic, and exposure can cause headaches, irritate the nose and throat (complaints which were reported in the Queensland study cited above), irritate the lungs, and damage the liver, kidneys and central nervous system, permissible exposure limits (PELs) have been set at 5.0 ppm over an eight-hour period. The need for a thorough risk assessment of gaseous emissions was particularly pronounced at the UCG site from where these samples were collected because the foul-smelling "rating 5" odour reported here for both wastewater and sludge was pervasive, making operations at the site particularly challenging.

CONCLUSIONS

To this author's knowledge, the present study represents one of the first published examinations of the chemical and odoriferous properties of underground coal gasification wastewater and sludge. While preliminary in nature, the findings confirm that UCG wastewater is contaminated with significantly high concentrations of benzene, alkanic hydrocarbons and phenols, and UCG sludge is similarly contaminated with benzene, toluene, ethylbenzene, xylene, alkanic hydrocarbons, arsenic and phenols. However, further research is required to better understand and document the potential environmental and human health effects, if any, of short-term and chronic exposure to these types of wastes. Large-scale field trials conducted with industry support should be undertaken and wellengineered treatment strategies with well documented and published results would help the international research community and general public better understand the relationship between UCG operations and health.

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