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Notes

Heat pumps as a tool for energy recovery from mining wastes

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Abstract: Heat pumps extract heat energy from a low-temperature source and transfer it to a higher temperature sink, usually via a closed loop of volatile 'refrigerant' fluid in a compression/expansion cycle. They can be efficiently used for space heating (and cooling), extracting heat from seawater, rivers, lakes, groundwater, rocks, sewage, or mine water. Electrical energy powers the heat pump's compressor. The ratio of total heat output to electrical energy input, called the coefficient of performance, typically ranges from 3.0 to 6.0. The use of mine water for space heating or cooling purposes has been demonstrated to be feasible and economic in applications in Scotland, Canada, Norway, and the USA. Mine water is an attractive energy resource due to: (1) the high water storage and water flux in mine workings, representing a huge renewable enthalpy reservoir; (2) the possibility of re-branding a potentially polluting environmental liability as a 'green' energy resource; and (3) the development of many mine sites as commercial/industrial parks with large space heating/cooling requirements. The exothermic nature of the pyrite oxidation reaction (>1000 kJ/mol) implies added benefits if closed-loop systems can harness the chemical energy released in mine-waste tips. An appreciation of geochemistry also assists in identifying and solving possible problems with precipitation reactions occurring in heat pump systems.

International conventions on emission of greenhouse gases have attempted to commit individual nations to decreased use of fossil fuels or, at the very least, decreased net emissions of carbon dioxide. It is recognized that no single new technology is likely to provide a complete solution to such issues and that a combination of policies is required, including: the development of renewable or non-fossil energy resources (biomass, wind, wave, solar, nuclear); increased efficiency of energy consumption; and alternative disposal routes for CO_2, other than mere atmospheric emission.

However, such courses of action are often significantly more expensive than continued use of fossil fuel. They have their own adverse environmental or aesthetic impacts (e.g., waste from nuclear power, visual impact of wind turbines). This paper discusses the use of heat pumps as a technology for efficiently transferring environmental heat (from the air, from water or from the ground) to the interior of buildings for purposes of space- or water-heating. In total, around 100 million heat pumps are installed world wide, with an annual capacity of 1300 TWh energy. They are estimated to result in a global saving in annual CO_2 emissions of 0.13 Gt, in the context of a global total CO_2 emission of 22 Gt (Bouma 2002). Specifically, this paper discusses the exploitation of *ground source heat* via heat pumps, and is largely based on a paper presented at a conference in Newcastle by Banks *et al.* (2003). This established and demonstrated technology has altered the pattern of energy usage in certain nations, such as Sweden, who have dared to invest in it. Ground source heat pumps essentially use electrical energy very efficiently to transfer renewable energy stored in rocks, water, or geogenic wastes to the user. This transferred energy may ultimately be:

- geothermal (derived from the Earth's natural geothermal gradient);
- solar (derived by solar heat warming up near-surface rocks and groundwater);
- chemical (derived from, for example, sulphide oxidation).

A recent Canadian assessment (Caneta Research 1999) concluded that, 'There is unlikely to be a potentially larger mitigating effect on greenhouse gas emissions and the resulting global warming impact of buildings from any other current, market-available single technology, than from ground source heat pumps.'

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Ground source heat

Groundwater has a huge capacity to store heat (4181 J/kg/K). Rocks and minerals have a lesser (around 800 J/kg/K; Mellon 2001), but still significant, heat capacity. They also have a certain thermal conductivity and these properties allow them to act as enormous subsurface heat storage and exchange reservoirs. Table 1 provides some examples of specific heat capacities and thermal conductivities. This heat, stored in the geological environment, can be extracted, manipulated and utilized.

At shallow depths, rocks and groundwater have an approximately constant temperature that roughly corresponds to the annual average air temperature. In Scandinavia, this may be as little as 4–7 °C, while in the southern UK temperatures of 10–12 °C are more typical. In the immediate subsurface (down to a few metres depth), some seasonal fluctuation will occur, with heat from the sun tending to warm the subsoil in the summer. The large heat capacity of the geological environment means that any seasonal variations are highly damped and that the subsoil is generally warmer than the air in winter. Conversely, it is generally cooler than the air in summer. At shallow depths, the stored heat energy is thus largely solar in origin. The Earth's surface acts, in effect, as an enormous solar collector.

At greater depth, stored heat energy in rocks and groundwater begins to have a larger geothermal component. The geothermal gradient varies from location to location at the Earth's surface and also varies with rock type (and thermal conductivity). Higher gradients are observed in areas of volcanic activity and crustal thinning. In general, however, gradients of 1–3 °C/100 m are common, reflecting a typical European geothermal heat flux of around 0.04–0.1 W/m^2. Thus, at the base of a typical British 100 m deep borehole, temperatures of around 13–14 °C may be expected.

Heat pumps may be used to extract some of this stored heat. The use of this 'ground source heat' was first proposed in 1912 in Switzerland, while

Table 1. *The thermal conductivity and specific volumetric heat capacity of selected rocks and minerals**

	Thermal conductivity (W/m/K)	Specific heat capacity (MJ/m^3/K)
Rocks		
Coal	*0.3*	*1.8*
Limestone	1.5–3.0 (*2.8, massive limestone*)	*2.3*
Shale	1.5–3.5 (*2.1*)	*2.3*
Wet clay	*1.6*	*2.4*
Basalt	*1.7*	*2.4*
Diorite	1.7–3.0 (*2.6*)	*2.9*
Sandstone	2.0–6.5 (*2.3*)	*2.0*
Gneiss	2.5–4.5 (*2.9*)	*2.1*
Arkose	*2.9*	*2.0*
Granite	3.0–4.0 (*3.4*)	*2.4*
Quartzite	5.5–7.5 (*6.0*)	*2.1*
Minerals		
Plagioclase	1.5–2.3	—
Mica	2.0–2.3	—
K-feldspar	2.5	—
Olivine	3.1–5.1	—
Quartz	7.7	—
Other		
Air	0.024	1.29×10^{-3} at 1 atm
Glass	0.8	—
Concrete	0.8 (*1.6*)	*1.8*
Ice	1.7 (*2.2*)	*1.9*
Water	*0.6*	4.18
Copper	390	3.5

*Data from inter alia Sundberg (1991), Banks & Robins (2002), Halliday & Resnick (1978). Italics show recommended values cited by Eskilson *et al.* (2000). Note that thermal conductivity increases with quartz content, and that most rock materials have a specific heat capacity of around 800 J/kg/K, or slightly over 2 MJ/m^3/K (compare with copper at only 386 J/kg/K).

the first applied research on heat pumps was carried out in the 1940s in the UK and USA (Rawlings & Sykulski 1999). This led, in 1948, to the installation in the UK of 12 prototype heat pumps with ground collectors, 9 kW output and a coefficient of performance (see below) as high as 3. It was not before the oil crisis of the 1970s, however, that the commercial use of ground source heat pumps (GSHPs) became widespread. Sweden, already with around 1000 GSHPs by the end of the 1970s, paved the way for much of the recent development of GSHPs, along with the USA, Austria, Switzerland, and Germany (partly due to government subsidies to assist in introducing and demonstrating the technology). In Sweden, for example, some 50 000 ground source heat plants were installed between 1980 and 1986, yielding about 500 MW of heat (Albu *et al.* 1997). Currently (Bouma 2002), over 90% of new Swedish houses are built with installed heat pumps, and 75% of such residential heat pumps are ground-sourced. Swedish heat pumps generate an estimated 7 TWh/y to district heating and a further 6 TWh/y to residential heating. In the USA, some 28 000 new GSHP units were installed annually in 1994, but by 1999 this total had risen to 50 000. In Canada, around 30 000 GSHPs were being installed annually throughout the 1990s, with 20% of this going to the commercial and institutional (e.g., school) sector (Bouma 2002). In the UK, although air-sourced (i.e., withdrawing heat from ambient air temperature) heat pumps are widely used (some 600 000 installed units), GSHP technology is almost unknown. Rawlings & Sykulski (1999) could find a mere ten examples in the UK, although the concept is rapidly gaining momentum, to the point where 150 new GSHP units were commissioned in 2001 (Table 2). Currently, around 500 000 GSHPs are believed to be installed world-wide, providing an estimated 6.7 GW energy, of which 4.8 GW are installed in the USA (Bouma 2002). These figures compare favourably with other 'alternative' energy sources. For example, the total-world installed wind energy capacity was 7.2 GW in 2002, whereas solar energy was <1 GW (BP 2003). However, these values are still of minor significance compared to the 'main players': consumption of coal accounted for 3190 GW, natural gas for 3040 GW, and oil for 4690 GW of power equivalent on average in 2002, with hydroelectric power weighing in at 790 GW, and nuclear power at 813 GW (BP 2003).

Table 2. *New ground source heat pumps sold in 2001, and annual growth rate in market, for selected European countries**

Country	Annual ground source heat pump sales (units/y)	Market growth rate for GSHPs (%)
UK	150	>100
Czech Republic	350	25
Poland	500	5
Norway	650	10
Switzerland	2800	6
Sweden	27000	6
Europe (total)	41000	

*After Bouma 2002.

Heat pumps

A heat pump is an electromechanical device that takes heat from a low-temperature medium (e.g., groundwater at, say, 7 °C in Norway) and transfers it to a high-temperature space-heating medium via a compression–expansion cycle. The space-heating medium may be air at, say, 25 °C (common in the USA) or the hot water of a household central heating system at 50–60 °C (common in Europe). The electricity consumed by the heat pump is used to 'push' the heat 'up' the temperature gradient (by powering the compressor). Many people find the concept of extracting heat from a cool medium intuitively problematic, yet the same people are comfortable enough with the concept of a domestic refrigerator. The refrigerator is, in fact, a heat pump: heat is extracted from a cool medium (the cool-box interior) and transferred to a warmer one (kitchen air). There are a number of different heat pump concepts (Fig. 1):

Open-loop systems. Groundwater is pumped from a borehole (or mine shaft) and circulated directly through the heat pump, which extracts heat directly from the water. This method is obviously appropriate where a significant water yield, with a suitable quality, can be achieved and maintained.

Closed-loop systems. In closed-loop systems, groundwater abstraction is not required. Such systems can be used in poorly permeable formations, such as hard rocks or clays. Closed-loop systems may be *direct circulation* where the heat pump refrigerant is pumped through a closed loop installed in the ground. More frequently they utilize *indirect* circulation. Here, water, usually with added anti-freeze (e.g., ethylene glycol or ethanol), is circulated through a closed polyethene hose system (the *collector*

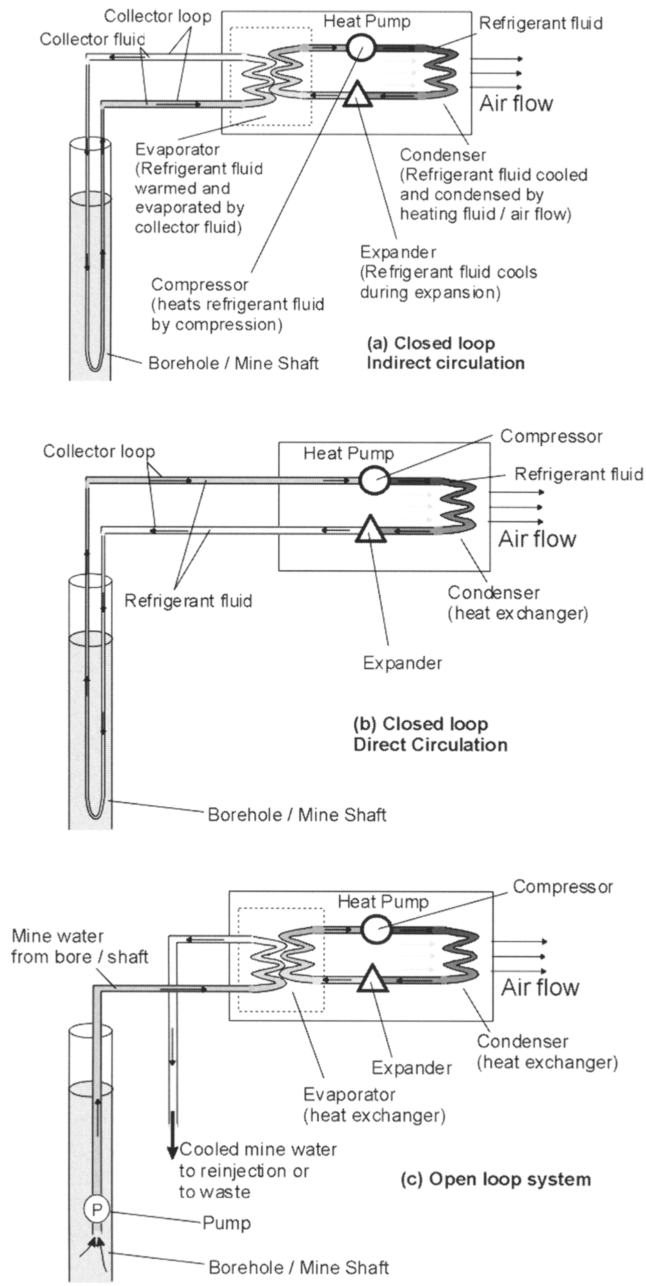

Fig. 1. Schematic diagrams of (**a**) a vertically installed, closed-loop, indirect circulation water-to-air heat pump. The collector fluid may be a solution based on glycol or ethanol mixture; the refrigerant may be hydrofluorocarbon (although use of many compounds may be limited by environmental legislation), hydrocarbon or ammonia-based (modified after Banks & Robins 2002). This type of system is well-suited to small-scale installations, installations in poor aquifers or aquitards (e.g., crystalline rocks, clays), or where water is of incompatible quality with a heat exchanger; (**b**) a closed-loop, direct circulation water-to-air heat pump. Here the refrigerant is circulated directly downhole; (**c**) an open-loop heat pump system, where the groundwater or mine water is passed directly through the heat pump. This is ideal for large-scale applications based on water from a good aquifer or mine system, where water quality is favourable. The water, once used, is either pumped to a suitable waste recipient, or re-injected to the aquifer or mine system. It may alternatively be used for 'grey water' applications, such as toilet flushing, if the water quality is suitable.

loop) in the ground. This may be installed *vertically* (down a borehole or shaft) or *horizontally* (e.g., below a grassed lawn, yard, or in a mine gallery). The fluid is warmed to the subsurface temperature and, on its return to the surface, may be sent through a heat pump.

The ratio of the total heat output of the heat pump to the quantity of electric energy input to the heat pump is called the *heat effect* or *coefficient of performance* (COP). This value depends on the temperature gradient, but is typically around 3–4 for an output temperature of 30 °C (and can be higher). Canada specifies a minimum COP of 3.0 for all ground source heat pumps rated below 35 kW (Bouma 2002).

As GSHPs are essentially transferring solar or geothermal energy, they can be regarded as environmentally sustainable, provided that the flux of energy extracted does not exceed the replenishment of energy in the ground from solar input or geothermal gradient. The only environmental drawback to heat pumps is that they require a certain electrical energy input to extract the ground source heat. However, the net energy benefit is huge, and savings in energy consumption in conventional heating outweigh the electricity consumed by heat pumps. Use of GSHPs powered by electricity generated by wind turbines can, assuming typical COP values, deliver heat to three to four times as many houses than if the heat power was generated by wind turbines alone.

Mines and mine wastes as sources for ground heat

It is possible to base heat pump systems on a variety of environmental media: seawater, unfrozen rivers, lakes, groundwater, rocks, or sewage. The one proviso for the efficient use of heat pumps is that the point of use must be relatively close to the source.

In ore- and coalfields, abandoned mines may be a particularly attractive energy resource, for several reasons. First, flooded, abandoned mines contain huge volumes of water at a relatively constant temperature. In other words, they are major reservoirs of stored enthalpy, which can be seasonally manipulated as sources or sinks for heat energy. Secondly, a mine system contains extensive areas (tunnels, working faces, mine waste, goaf) where flowing groundwater is in contact with rocks. The mine is thus a major heat-exchanger between a storage medium (rocks and minerals) and a transport medium (flowing groundwater). Thirdly, where flooded mines overflow at the surface, gravity drainage from mines may yield considerable quantities of water at a constant temperature that can be used in heat pumps with minimal consumption of energy for pumping. Fourthly, even where gravity drainage does not exist, boreholes can be drilled into old mine workings. Open- or closed-loop systems can then be installed in these boreholes or existing shafts. The large quantities of water travelling through disused workings ensure that the available energy is renewed by convection as well as by thermal conduction. The size and complexity of some mine workings mean that different parts of a mine system may have differing thermal properties and can be used for extracting heat and for cooling purposes, respectively. Fifthly, in deep mines, there may be a substantial geothermal component to the temperature, as well as the solar component, adding to the efficiency of the system. Finally, and crucially, many mining areas in Western Europe and North America are gradually being abandoned, and are often the recipients of grants to stimulate new 'brownfield' development and industry. New commercial and industrial parks, with demands for environmentally friendly and economically efficient space heating and cooling are thus currently being planned or constructed in the vicinity of flooded mines in these areas. The developments may even occur at the mine head sites themselves, where mine-waste tips may be located or where existing shafts may facilitate access for heat pump systems to mine water reservoirs.

Groundwater or mine water may not only be used for heating, but also to cool offices, communal spaces, or areas with a high density of heat-generating equipment (e.g., computers, telephone exchanges). This is often most efficiently done by direct 'free cooling'. Here, heat migrates from a building interior to circulating groundwater via a system of heat exchangers with high surface area. Use of chilled beams or panels can result in the establishment of convection cells in a room. The 'direction' of heat pumps can also be reversed, leading to 'active chilling' of a space, such that heat is transferred from a building interior to an environmental recipient (air, water, rock). 'Waste' heat from space-cooling applications may be re-used to heat other parts of a building complex. Alternatively, it may be re-injected to the groundwater body (Morgan 1997), possibly to be re-extracted and be used later (e.g., in winter).

Geochemistry and mine water heat pumps

Geochemistry is relevant to the concept of using heat pumps in mine systems from three perspectives: (1) the generation of contaminant fluxes by sulphide oxidation in mine systems, which may require treatment – recovery of energy can assist in offsetting the costs of treatment; (2) exothermic sulphide oxidation reactions can boost the efficiency of heat extraction systems; and (3) mine water may have a tendency to precipitate oxyhydroxide (or other chemical) deposits, which will require special consideration to avoid fouling of circulation pipes and exchangers.

Mine water: hydrochemical liability or environmental asset?

Many metalliferous ore deposits and most coalfields are characterized by the presence of sulphide minerals, such as pyrite (FeS_2), galena (PbS), or sphalerite (ZnS). When exposed to water and oxygen, these sulphides have a tendency to oxidize, releasing dissolved metals, sulphate and, in the case of pyrite, acid (equations 1 and 2).

$$2\,FeS_2 + 7\,O_2 + 2\,H_2O = 2\,Fe^{2+} + 4\,SO_4^{2-} + 4\,H^+ \quad (1)$$

$$ZnS + 2\,O_2 = Zn^{2+} + SO_4^{2-} \quad (2)$$

Table 3 illustrates the composition of four mine waters. It will be noted that sulphide ore mines tend to generate more aggressive mine water than coal mines, and that recently flooded mines tend to generate poorer water qualities than long-abandoned mines (Banks *et al.* 1997*b*). Of the mines detailed in Table 3, the Dunston and Morlais mine waters are being or planned to be treated by passive settlement/wetland systems (Banks & Banks 2001; Younger, 2004). Kongens mine, Røros, is being assessed for possible treatment using electrolysis, active treatment and/or anaerobic cells (Banks *et al.* 1997*b*; Iversen & Knudsen 1997; Ettner 2002). The San José mine (Banks *et al.* 2002) area is the subject of intense planning for remediation of mine water and mine wastes: a favoured option for mine water treatment involves evaporation.

Further oxidation of ferrous iron (Fe^{2+}) to ferric (Fe^{3+}) may take place, followed by hydrolysis and precipitation of Fe^{3+}-oxyhydroxides:

$$2\,H^+ + 2\,Fe^{2+} + \frac{1}{2}O_2 = 2\,Fe^{3+} + H_2O \quad (3)$$

$$2\,Fe^{3+} + 6\,H_2O = 2\,Fe(OH)_3 + 6\,H^+ \quad (4)$$

Because of the elevated concentrations of potentially ecotoxic metals and acid in mine water, and because of the potential for precipitation of benthos-smothering Fe, Al, Mn-oxyhydroxides (and other phases) in downstream recipient watercourses, water draining from mines is often regarded as a major environmental problem. Considerable effort and expense are incurred by treating

Table 3. *Composition of four selected mine waters to illustrate possible range in composition*

	Mine			
	Dunston (Fender)	Morlais	Kongens Gruve	San José
Location	Chesterfield	nr. Llangennech	Røros	Oruro
Region	Derbyshire	South Wales		Altiplano
Country	UK	UK	Norway	Bolivia
Type of mine	Long-abandoned coal mine; overflowing shaft	Coal mine, flooded by 1986; overflowing shaft	Cu–Zn sulphide mine; overflowing via adit	Pumped Ag–Sn mine
Source	Banks *et al.* (1997*a*) Banks & Banks (2001)	Unpublished Coal Authority data	Iversen & Knudsen (1997)	Banks *et al.* (2002)
Flow rate (L/s)	*c.* 20	*c.* 100–200	5.8 (average)	8
Temperature (°C)	9.4	14.2	n/a	20.8
pH	6.3	6.9	2.7	1.47
Alkalinity (meq/L)	3.74	6.07	0	0
Cl^- (mg/L)	26	25	n/a	32670
SO_4^{2-} (mg/L)	210	455	901	8477
Ca^{2+} (mg/L)	64.5	91.8	47.8	1780
Na^+ (mg/L)	51.4	155	n/a	17256
Fe (mg/L)	10.6	26.6	134	2460
Al (mg/L)	<0.045	<0.01	33.1	559
Mn (mg/L)	1.26	0.93	n/a	27.4
Zn (mg/L)	<0.007	<0.002	36.3	79.4

such waters, either by active or passive methods (see Younger *et al.* 2002; Younger, 2004).

However, some of these mine waters have significant potential for energy recovery via use of heat pumps. For example, the Morlais mine water of South Wales has an estimated discharge of at least 100 L/s. The specific heat capacity of water is around 4181 J/L/°C or 1.16 kWh/m^3/°C. If the Morlais mine water's temperature could be lowered by using a heat pump by 5 °C (from 14 to 9 °C), a heat flux (power) of:

$$100\,\mathrm{L/s} \times 4.2\,\mathrm{kJ/L/^{\circ}C} \times 5\,^{\circ}\mathrm{C} = 2100\,\mathrm{kW}$$

could be removed. Assuming a COP of 3.5, the energy input to drive an (admittedly rather large) heat pump array would be around 840 kW, yielding a total effect of 2.94 MW for heating purposes. A similar calculation for the 20 L/s Dunston mine water would yield a total heat effect of 470 kW (Banks *et al.* 2003). Clearly, these are theoretical calculations: one would need a heat pump array of adequate capacity and efficiency to harness this energy and, not least, one would need nearby consumers to consume the heat energy produced. Abandoned mine sites are, however, extremely attractive areas for new commercial and industrial developments. The effective harnessing of energy from mine water, either from naturally overflowing mines or pumped shafts/boreholes, can turn an environmental liability (mine water) into an environmental asset (a clean energy source). Provision of energy can also help in recouping the costs of mine water treatment.

Harnessing exothermic reactions

Sulphide oxidation is typically a highly exothermic reaction, and is typically microbiologically catalysed by bacteria such as *Thiobacillus ferrooxidans*. Norwegian miners were familiar with the phenomenon of the *kisbrann* or spontaneous combustion of sulphide minerals. The continued exothermic oxidation of pyrite minerals is evidenced by the excessive down-mine temperatures in, for example, the Norwegian Killingdal Cu–Zn–Fe–S mine (Banks 1994). At the Richmond Mine, Iron Mountain, California (Banfield & Gihring 2003), in-mine temperatures of 35–50 °C are reached. Within mine-waste tips and tailings deposits of sulphide mines, interior temperatures in excess of several tens of degrees have been recorded (e.g., over 50 °C at San José mine in Oruro; Banks *et al.* 2002), with values of up to 70 °C in extreme cases (Wels *et al.* 2003). Even at Killingdal, where the annual average air temperature is around 0 °C, exothermic reactions maintain the interior temperature of mine-waste tips at around 10 °C or above (Iversen 1998). Spontaneous combustion (often initiated by pyrite oxidation (Stevens 1869), and maintained by combustion of coal) is also a recognized phenomenon in coal mines, coal stores, and coal spoil tips (Younger, 2004). Sulphide oxidation is also known to initiate the combustion of oil shales on the UK's Dorset Coast (West 2001).

An indication of the degree of exothermicity of sulphide oxidation reactions can be gained by comparing the enthalpy of formation (ΔH_f°), that is, a measure of the energy locked up in each chemical species, relative to native elements. The difference in enthalpies of formation of all reactants and all products defines the enthalpy (heat released or absorbed) of the reaction. Thermodynamic data on sulphide minerals, such as pyrite, are notoriously varied and disputed, and the values in Table 4 must be treated with caution. Nevertheless, depending on whether one defines the reaction as ending in an aqueous solution (equation 5), an intermediate secondary sulphate (e.g., melanterite – equation 6) or in complete oxidation to an oxyhydroxide (equation 7), the calculated reaction enthalpy (ΔH_r°) released is of the order of at least 1000 kJ/mol.

$$\mathrm{FeS_2} + \frac{7}{2}\,\mathrm{O_2} + \mathrm{H_2O} = \mathrm{Fe^{2+}} + 2\,\mathrm{SO_4^{2-}} + 2\,\mathrm{H^+} \quad (5)$$

$$\begin{aligned}\Delta H^\circ_{f(\mathrm{Reactants})} &= -178 - 286 = -464\,\mathrm{kJ/mol}\\ \Delta H^\circ_{f(\mathrm{Products})} &= -90 - 1818 = -1908\,\mathrm{kJ/mol}\\ \Delta H^\circ_r &= -1444\,\mathrm{kJ/mol}\end{aligned}$$

$$\begin{aligned}\mathrm{FeS_2} + \frac{7}{2}\,\mathrm{O_2} + 8\mathrm{H_2O} &= \mathrm{FeSO_4}\cdot 7\,\mathrm{H_2O}\\ &\quad + \mathrm{SO_4^{2-}} + 2\,\mathrm{H^+} \qquad (6)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{f(\mathrm{Reactants})} &= -178 - 2288 = -2466\,\mathrm{kJ/mol}\\ \Delta H^\circ_{f(\mathrm{Products})} &= -3013 - 909 = -3922\,\mathrm{kJ/mol}\\ \Delta H^\circ_r &= -1456\,\mathrm{kJ/mol}\end{aligned}$$

$$\begin{aligned}\mathrm{FeS_2} + \frac{15}{4}\,\mathrm{O_2} + \frac{7}{2}\,\mathrm{H_2O} &= \mathrm{Fe(OH)_3}\\ &\quad + 2\,\mathrm{SO_4^{2-}} + 4\,\mathrm{H^+} \qquad (7)\end{aligned}$$

$$\begin{aligned}\Delta H^\circ_{f(\mathrm{Reactants})} &= -178 - 1001 = -1179\,\mathrm{kJ/mol}\\ \Delta H^\circ_{f(\mathrm{Products})} &= -823 - 1818 = -2641\,\mathrm{kJ/mol}\\ \Delta H^\circ_r &= -1462\,\mathrm{kJ/mol}\end{aligned}$$

Table 4. *Enthalpies of formation of selected species involved in sulphide oxidation reactions*

Reactants		Products	
Species	kJ/mol	Species	kJ/mol
O_2(g)	0[d]	Pb^{2+}(aq)	−1.7[b]
O_2 (aq)	−12[b]	Fe^{3+}(aq)	−49[a]
H_2O (l)	−286[f]	Fe^{2+}(aq)	−90[a]
H_2S (g)	−21[f]	Zn^{2+}(aq)	−154[b]
Covellite, CuS	−53[b]	Anglesite, $PbSO_4$	−920[b]
Chalcocite, Cu_2S	−80[b]	$FeSO_4$	−932[a]
Galena, PbS	−100[b]	Rozenite, $FeSO_4.4H_2O$	−2129[a]
Pyrrhotite, FeS	−100[b]	Bianchite, $ZnSO_4.6H_2O$	−2778[a]
Troilite, FeS	−102[e]	Melanterite, $FeSO_4.7H_2O$	−3013[a]
Marcasite, FeS_2	−172[e]	Coquimbite, $Fe_2(SO_4)_3.9H_2O$	−5288[a]
Pyrite, FeS_2	−167[e]	Römerite, $Fe^{II}Fe_2^{III}(SO_4)_4.14H_2O$	−7730[a]
Pyrite, FeS_2	−178[b]	Halotrichite, $FeAl_2(SO_4)_4.22H_2O$	−11041[a]
Sphalerite, ZnS	−206[b]		
		$Fe(OH)_3$ crystalline	−823[b]
		$Al(OH)_3$	−1276[b]
		H^+(aq)	0[d]
		SO_4^{2-}(aq)	−909[b]

*Enthalpies are cited in kJ/mol at 25 °C and 1 bar. Note: pyrrhotite is cited as an idealized FeS phase. In reality, pyrrhotite has a formula $Fe_{1-x}S$, where x ranges from 0 to 0.17. The pure FeS mineral, troilite, does not exist in nature on the Earth's surface and is found in meteorites.

[a]Hemingway *et al.* (2002); [b]USNBS (1982); [c]Cox *et al.* (1989); [d]base state; [e]Chase (1998); [f]Moore (1972).

Wels *et al.* (2003) cite an exothermic energy release upon pyrite oxidation of 1409 kJ/mol pyrite, equating to 11.7 kJ/g pyrite. Of course, the rate of release of heat in kW from a waste tip will depend on physicochemical factors such as grain size (exposed surface area), permeability of the mass to O_2, and also on the activity of the bacteria that catalyse the redox reactions involving Fe and S.

For other minerals, such as pyrrhotite (and, in Table 4, an ideal composition of FeS is assumed, rather than the more realistic $Fe_{1-x}S$), galena or sphalerite, the following equations may apply:

$$FeS + O_2 = Fe^{2+} + 2SO_4^{=} \qquad (8)$$

$$\begin{aligned}\Delta H^\circ_{f(\text{Reactants})} &= -100 - 0 = -100\,\text{kJ/mol}\\ \Delta H^\circ_{f(\text{Products})} &= -90 - 1818 = -1908\,\text{kJ/mol}\\ \Delta H^\circ_r &= -1808\,\text{kJ/mol}\end{aligned}$$

$$ZnS + O_2 = Zn^{2+} + 2SO_4^{=} \qquad (9)$$

$$\begin{aligned}\Delta H^\circ_{f(\text{Reactants})} &= -206 - 0 = -206\,\text{kJ/mol}\\ \Delta H^\circ_{f(\text{Products})} &= -154 - 1818 = -1972\,\text{kJ/mol}\\ \Delta H^\circ_r &= -1766\,\text{kJ/mol}\end{aligned}$$

In the case of coals, the energy released upon thermal oxidation will depend on the sulphide content, the calorific content of the coal (typically ranging from 14 MJ/kg (lignite) to > 33 MJ/kg (anthracite); Wood *et al.* 1983), and the extent of oxidation (whether incomplete to CO, or complete to CO_2).

The energy released by exothermic reactions (such as equations 5 to 9) could be efficiently recovered from mine-waste tips using heat pumps or exchangers. Closed-loop coils of suitable materials could be buried within the wastes and water circulated as a collector fluid. The collector fluid could be passed via a heat pump to boost temperature or, in extreme cases where temperature was already sufficiently high, used directly for space heating via heat exchangers. In Oruro, Bolivia, for example, 'hot' mine-waste deposits (sometimes >50 °C) occur in the immediate proximity of residential dwellings and public buildings in the high, seasonally cold Altiplano city (with average monthly temperatures ranging from 5 to 13 °C), with its significant energy demands and a limited energy supply.

Fouling of heat pump/exchanger elements

In the context of use of mine water for space heating and cooling purposes, concern is often expressed as to the possibility of fouling of pipework and exchanger elements by precipitation of secondary minerals such as Fe-oxyhydroxides (equation 4) or other hydroxide or, conceivably, carbonate minerals. This concern is valid, but several methods are available for dealing with the problem:

(1) Use closed-loop systems, which might be installed 'down-mine', or within settlement basins at a minewater treatment plant. Here the collector fluid circulates in a closed-loop and never comes into contact with the mine water. Likewise, mine water never enters the heat pump or heat exchanger elements. The problem is thus wholly averted, although there are limitations in capacity to closed-loop systems. For larger capacity operations, open systems will be preferred. Furthermore, the exterior of such closed-loop systems may become heavily fouled, necessitating periodic removal for cleaning.
(2) Where open-loop systems are unavoidable, mine water should be circulated through heat pumps and exchangers in such a way as to minimize contact with atmospheric O_2, which promotes oxidation of Fe^{2+} to poorly soluble Fe^{3+}. Also consideration should be given to pressurized systems, in which down-mine pressures are maintained as far as possible, to hinder degassing of, for example, CO_2. Such degassing may elevate pH and promote precipitation of Fe-oxyhydroxides or carbonate scales.
(3) A range of mechanical techniques are available to de-scale pipes and exchanger surfaces. High pressure jetting of the interior of a pipe circuit may be sufficient to remove loose chemical precipitates. The use of acids in jetting might also be considered to redissolve hydroxide precipitates, provided that their compatibility with pipe circuit and exchanger components has been considered. Pigging involves the insertion of a cylindrical tool (a 'pig') into a pipe. Different 'pigs' may be used for inspection, scouring or abrasion of the interior surface of the pipe. The addition to minewater pipelines of phosphate-based dispersing agents to break up precipitates, or reducing agents (such as sodium dithionate) to scavenge oxygen, are also being trialled (Dudeney *et al.* 2002).

Sustainability and kinetics

The question naturally arises as to the sustainability of mine-based heat pump systems: are we removing more heat from the ground than is naturally replenished by solar energy, the geothermal gradient or exothermic reactions? In other words, can we overabstract a heat reservoir?

Underground mines

The physics of thermal conduction and storage are, in fact, directly analogous to those of groundwater flow. Thermal conductivity (k_T) and hydraulic conductivity (k) are analogous, as are heat capacity and storage coefficient; and temperature (T) and hydraulic head (h). Indeed, heat flow (H) is estimated by an analogous equation to Darcy's Law:

$$H = -k_T \times A \times dT/dx \tag{10}$$

$$Q = -k \times A \times dh/dx \quad \text{(Darcy's Law)}, \tag{11}$$

where Q is groundwater flow, A is cross-sectional area, and x is a distance coordinate).

The sustainable yield of groundwater from an aquifer depends ultimately on recharge from rainfall and other sources. It also depends on how efficiently the aquifer and the borehole can capture that recharge (i.e., develop a 'well catchment area'), and thus on aquifer properties such as hydraulic conductivity and storage. Similarly, the sustainable heat yield of a shallow borehole-based heat pump system will depend on input of solar energy to the geological environment (and also geothermal gradient and exothermic reaction rates, typically in that order of importance), thermal conductivity and heat capacity. However, many of these parameters exhibit relatively low variability (Table 1), thus permitting the application of standard dimensioning 'rules of thumb' for small heat pump systems in hard, crystalline rock aquifers.

The physics of subsurface heat flow differs from that of groundwater flow in one important aspect, however. In aquifer strata, heat is not transported just by thermal conduction in proportion to the temperature gradient and thermal conductivity. It can also be transported by convection; that is, heat stored in groundwater is transported by groundwater flow. Thus, a heat pump system installed in a flowing system (an aquifer or a large mine) will often be able to extract greater sustainable heat yields (and develop a greater thermal catchment) than those installed in low-permeability crystalline rock, due to subsurface heat flow by convection as well as conduction.

In most flooded mine systems (including all the case studies mentioned below), the ultimate source of heat will be either solar energy input to the geological environment from the surface or, in deeper mines, the geothermal gradient. The energy input from exothermic oxidation reactions will typically be relatively low: the bacterially catalysed sulphide oxidation reaction requires a large flux of oxidizing species (in practical terms, the presence of gas-phase O_2) to progress at a significant rate. Sulphide oxidation will thus only typically be significant in terms of heat flux above, or within the zone of fluctuation of, the water table. Below the water table in flooded mines, the rate of sulphide oxidation is severely limited by the solubility of O_2. Indeed, flooding of mines, or underwater disposal of mine wastes, is a recognized method of suppressing acid rock drainage generation (Banks *et al.* 1997*b*). Thus, the design of heat pump systems for underground flooded mine systems requires, first and foremost, a good understanding of the hydraulics and groundwater throughput of the mine system. This will typically be mine-specific, and a considerable volume of literature is available concerning such hydraulic characterization (see, for example, Younger & Robins 2002; Younger *et al.* 2002).

Mine-waste tips

The use of heat pumps to harness the heat generated by exothermic reactions in mine-waste tips, however, remains largely undemonstrated. Here, clearly, a thorough understanding of geochemical processes and, in particular, kinetics, will be important to be able to assess sustainable rates of heat extraction. However, as the sulphide oxidation reaction generates heat in proportion to generation of contaminants (metals, acid, sulphate; e.g., equations 1 and 2), it should be possible to apply the results of the large volume of research on the kinetics of generation of acid rock drainage (e.g., Strömberg & Banwart 1994, 1999; Banwart *et al.* 2002) to sulphide-dominated mine-waste tips. The primary controls on rate of the pyrite oxidation reaction are (Banwart *et al.* 2002; Banks *in press*):

- mass of pyrite present in waste rock;
- specific surface area of pyrite (i.e., grain size);
- concentrations of reactants (O_2, Fe^{3+}) – the abiotic rate of reaction increases as concentrations increase;
- bacterial activity (sulphide oxidation reactions are bacterially catalysed), which may, in turn, be influenced by nutrient concentrations and temperature; while abiotic pyrite oxidation typically has a rate of 10^{-9} to 10^{-10} mol/m^2/s at pH 7 (Younger *et al.* 2002), bacterially mediated pyrite oxidation may be 25–34 times faster than abiotic oxidation. Bacterially mediated Fe^{2+} oxidation (equation 3) may be 10^6 times faster than abiotic oxidation;
- temperature (abiotic rate decreases with temperature);
- pH (abiotic rate decreases as pH decreases). However, *Thiobacillus ferrooxidans* thrives at a pH range of 1.5–3.0 and, at low pH values, bacterially mediated oxidation will overwhelmingly dominate abiotic oxidation.

Thus, the *a priori* estimation of sulphide oxidation rates (and thus of heat generation) in many coarse metals mine-waste tips will be almost impossible, requiring a quantification not only of three-phase (gas, water, solid) geochemical processes but also of microbiological activity, and the flux of O_2 through the wastes (convection as well as diffusion). In such cases, the most practical approach may simply be reverse modelling: inferring rates of reaction from fluxes of reaction products (e.g., $SO_4^=$) from the waste tip. This should, however, be tempered by an understanding that extraction of heat will change the temperature within a waste tip, which will in turn affect abiotic reaction rate, microbiological activity, and the convection of air through coarse-grained wastes.

In the case of mine waste comprising finer grained tailings, a theoretical approach to calculating exothermic reaction rates can be tractable, as the diffusion of O_2 into the wastes may be a rate-limiting step, and a process that can be simulated by relatively straightforward models.

Longevity

For heat pumps based on flooded mine systems, where the heat abstracted is replenished seasonally by inputs from solar radiation and geothermal gradient, the longevity of the reservoir is, in principle, limitless. The sustainability of the operation will only be limited by the durability of the infrastructure (e.g., biofouling, clogging or physical instability of boreholes, longevity of collector coils).

For heat pumps based on the exothermic oxidation reactions taking place in mine-waste tips, the longevity of the operation will be limited by the mass of reactant (sulphide or organic carbon/coal) within the waste. However, if the principles above are applied and the reaction rates within the waste deduced, the longevity of the exothermic reactants can be estimated (see, e.g., Strömberg & Banwart 1994, 1999). In practice, however, many mine-waste tips are estimated to have a sulphide oxidation longevity of decades or centuries (Younger *et al.* 2002).

Case studies

Four case studies will be presented to demonstrate that mine-water-based heat pumps are not 'pie-in-the-sky', but technology that has been demonstrated to be functional, economically advantageous, and environmentally friendly. Further details may be found in the paper by Banks *et al.* (2003).

Metals mines: 1, Park Hills, Missouri, USA

At this site (Heat Pump News 1996; CADDET 2000), water is extracted from workings between 11 and 133 m below ground level in abandoned and flooded Pb mines and has been used to heat and cool the Municipal Building (area 753 m^2) since 1995. The minewater, at a temperature of 13.9 °C, is abstracted at 4.7 L/s via a 122 m deep well and is passed through a plate heat exchanger, which transfers heat to a closed-loop water system. This, in turn, feeds nine water-to-air heat pumps for space heating. The mine water is re-injected via a second well. In the summer, the building can be cooled by reversing the whole system. The system cost US$132 400 (GBP£72 800 at current rates) to install, some $22 200 more than a conventional system. The annual savings, compared with a conventional system, are estimated as US$4800, resulting in a payback time of 4.6 years.

Metals mines: 2, Folldal and Kongsberg, Norway

Folldal is located in Central Norway (Fig. 2) and has operated a mine since 1748. Mining for Cu, Zn, and S continued for almost 200 years, and a community became established around the mine. After 1941, however, the main production shifted to other mines, including Hjerkinn, some distance away in the Dovre Mountain massif.

At the original Folldal mine, the underground Wormshall cavern is still used for concerts and banquets. Since October 1998, it has been heated by a heat pump system based on mine water. A 600 m long, 50 mm diameter closed-loop collector pipe is installed in a 600 m deep flooded shaft. This feeds a heat pump running off 4.6 kW electrical energy and delivering warm air at 22 °C, with a space-heating effect of 18 kW (Åge Kristoffersen, Folldal mine, personal communication). The total installation cost is reported to be some 150 000 NoK (GBP£12 000).

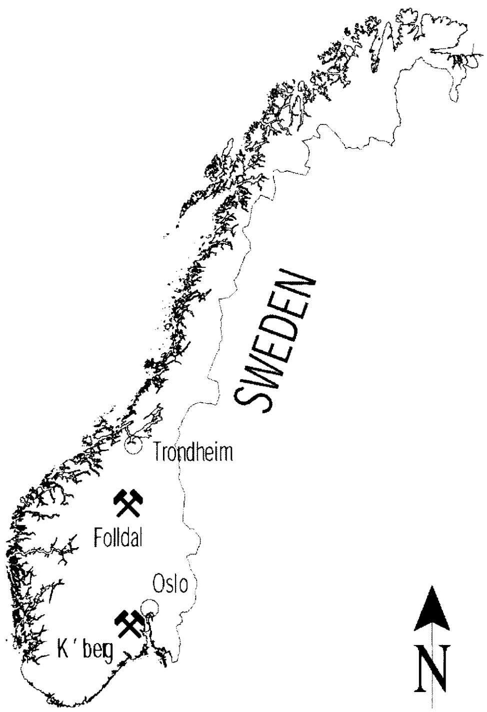

Fig. 2. Overview map of Norway, showing locations of Folldal mine and Kongsberg mine, together with the two major cities of Trondheim and Oslo.

A similar system is being planned by researchers at Buskerud College (Hostvedt *et al.* 2002) at the Kongsberg Silver Mine of southern Norway (Fig. 2), which has a working history stretching back several centuries. Since 1957, however, it has only been active as a tourist site, comprising a mining museum and an underground banqueting and concert hall (the 'Festsalen', located some 342 m below ground level). Most of the various mine complexes of Kongsberg are linked at the Christian VII adit level at 200 m above sea level. This also represents the lowest mine drainage level and the workings below it are flooded (Fig. 3). Even in summer, the air temperature around the Festsalen does not exceed 6 °C, despite a rock temperature of c. 9 °C, as density-driven air currents enter the mine via an upland entrance. The Festsalen thus requires heating in order to be a comfortable venue.

Fortuitously, the Festsalen is located near the flooded main mine shaft, at the base of which temperatures are believed to be as high as 16.4 °C. A proposal for an open-loop heat

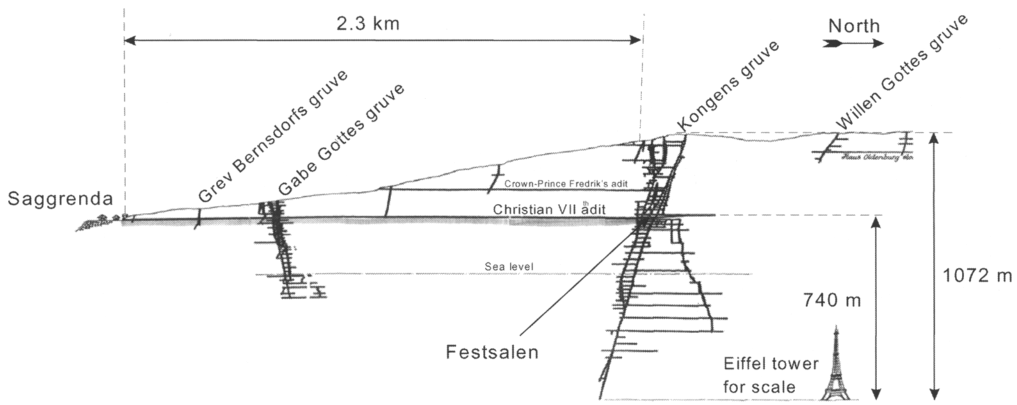

Fig. 3. Cross-section through the Kongsberg mine complex, showing the location of the Festsalen in Kongens Gruve (not to be confused with the mine of the same name at Røros, Table 3), approximately at the coincidence of the main lift shaft and the Christian VII adit (after Hostvedt *et al.* 2002).

pump scheme was rejected due to concerns over compatibility of water quality with heat exchangers. Planning has continued on the basis of an indirect closed loop system (Fig. 4). It is proposed that an anti-freeze fluid would circulate through a closed polyethene collector loop with a pipe length of 130–250 m installed in the main shaft. This system is dimensioned to be able to collect some 12 kW (of the mine's peak demand of 15 kW) heat energy, raising the temperature of the collector fluid to some 10 °C. This temperature would be elevated by passage through a water–water heat pump, to 35 °C. Of this output, 20% would serve a water–air

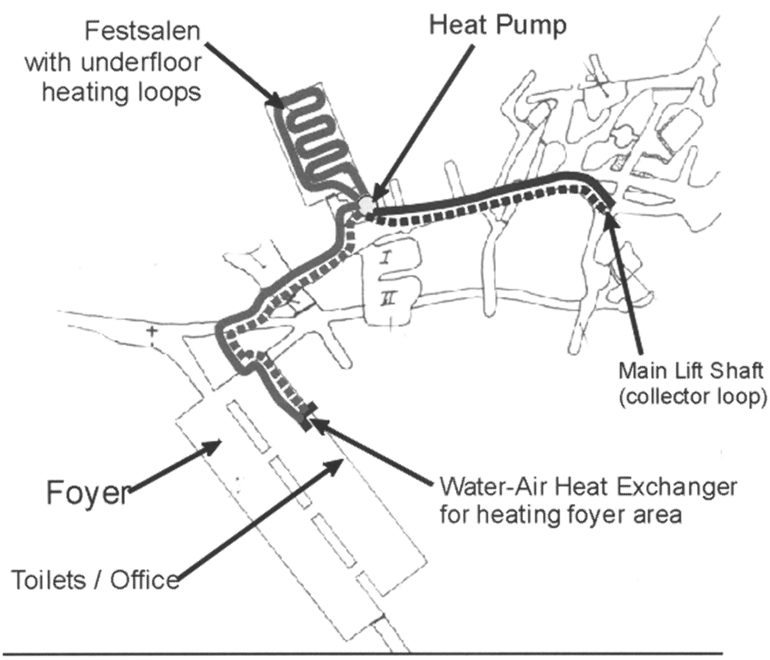

Fig. 4. Schematic plan of the closed-loop scheme to heat the Kongsberg Festsalen. The collector loop is installed in the main lift shaft, and the heat pump outside the Festsalen. The heat pump feeds an underfloor heating loop in the Festsalen and a water–air exchanger in the peripheral areas (after Hostvedt *et al.* 2002).

exchanger, heating the Festsalen's access areas and vestibule, and 80% would heat the Festsalen itself via underfloor loops. The scheme is estimated to cost NoK 81 950 (or c. GBP£7000, of which the heat pump accounts for NoK 42 800, or GBP£3500), and to result in energy savings of NoK 39 000 (or GBP£3100) per year. The payback time for the total cost of the scheme is thus around 2.3 years.

There are also tentative proposals to extend a collector hose from another part of the mine to satisfy the heating requirements of the Mining Museum's topside complex and the State Forestry School at Saggrenda (Fig. 3).

Coal mines: 1, Springhill, Nova Scotia, Canada

At this site (CADDETT 1992, 1997), an industrial plastic packaging plant with an effective area of 13 500 m^2, was retrofitted with 11 heat pumps. These used coal-mine water as a source for all the plant's cooling and heating requirements. Mine water, with a temperature of 18 °C, is pumped from 140 m depth at a rate of 4 L/s. The GSHPs extract heat and lower the water temperature to 13 °C. The mine water is returned to a shallower level (30 m depth) in the mine system. In the summer, the heat pumps are reversed and heat is extracted from the warm air of the building and transferred to the mine water, which is returned to the mine system at 23 °C. The cost of the system was reported to be some Can$110 000 (GBP£47 000 at current rates). A conventional propane-based heating system was estimated to cost Can$70 000 (GBP£30 000). The heat-pump based system resulted, however, in a reported annual energy saving of Can$45 000 (GBP£19 000). These figures imply a payback time of the capital difference of around only 1 year.

Coal mines: 2, Shettleston and Lumphinnans, Scotland

The firm John Gilbert Architects (1999, 2001*a*, *b*) has been involved in the design of two mine water-based heat pump systems in Scotland. The first was completed in 1999 in Shettleston, Glasgow, serving 16 newly built dwellings. The heating system uses water from 100 m depth in a flooded coal mine underlying the housing site. The 12 °C mine water circulates through a water-to-water heat pump, and is thereafter returned to the groundwater body at 3 °C. Alternatively, this 'waste' mine water can be used as 'grey water' for flushing toilets. The heated water output from the heat pump at 55 °C is then transferred to a thermal storage tank, with a side loop to 36 m^2 solar collector panels, which further contribute to the stored enthalpy. This storage tank supplies both central heating systems and hot water immersion heaters for individual dwellings. The total annual heating cost per home is estimated at only GBP£19–30, while the hot water cost is estimated as GBP£55–60.

Another similar scheme is operational at Ochil View, Lumphinnans, Fife, where the heat pump system was retrofitted to 18 dwellings. Water is pumped from a flooded coal mine beneath the site at 170 m depth and utilized via water-to-water heat pumps in a similar manner to Shettleston (although without the solar collectors to boost energy input). The project was completed in August 2001.

Furthermore, a major new town development around the former 1000 m deep Monktonhall Colliery in Midlothian, Scotland, is in the planning stage. Mine water is being seriously assessed as a possible source of heating and cooling requirements for the town, whose peak heat energy demand could reach 30 MW (ENDS 2002).

Conclusions

Wastes from both coal and metals mining (mine water, waste rock, and tailings) represent potential reservoirs of heat energy that can be utilized with the assistance of modern heat-pump technology. Heat pumps based on mine water and mine waste are an extremely attractive proposition because: (1) they can represent a potentially genuinely competitive energy source, especially for large buildings/industrial estates (although this obviously depends on energy policy and pricing in the country concerned); and (2) they convert an environmental liability (a mine water) to an environmental asset (a renewable energy source).

It is, however, reasonable to ask why, if mine waters and wastes represent such an attractive source for heat pumps, larger numbers of such systems have not been installed. In great part, the authors would argue that this is due to lack of awareness on the part of developers and potential users, and their risk-averse attitudes to new technology that may not be regarded as having been adequately 'proven'. Additionally, relatively low energy prices in certain countries (e.g., electricity, until recently, in Norway; mains gas in the UK) have discouraged developers from adopting poorly known alternative technologies. Other potential disadvantages that may be cited by sceptics include: (1) the fact that such systems (like other 'alternative' technologies, such as solar cells or panels) require an initially large capital investment, rendering them unattractive in the short term to small-scale users (although still competitive for large users, with payback times as short as one to two years); and (2) heat exchangers may be liable to fouling by precipitates from mine water in open-loop systems (but technological solutions are available). Closed-loop systems will be more robust in this respect, though these are limited in the energy output, and even these may require periodic removal of mine-water-related precipitates.

Moreover, mine-water-based heat pump systems have been installed in Canada, the USA, Scandinavia, and Scotland, and have been demonstrated to be a realistic alternative space-heating and -cooling solution.

Finally, it should be noted that regulations surrounding the implementation of ground source heat pumps are unclear. Any organization considering the installation of a mine-based heat pump should contact the relevant mining, environmental, and water authorities to obtain the necessary drilling, abstraction, and discharge permits. In the UK, this includes the Environment Agency and the Coal Authority.

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