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The freeze desalination of mine waters*

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SYNOPSIS

Consideration is given to the technical and economic feasibility of freeze desalination as a technique for the simultaneous provision of ice to cool deep mines and for the desalination of mine water.

Freeze desalination has not been developed fully or commercially. For sea-water applications, it may not offer significant advantages over other methods of desalination but, for the unique mining application, a single dual-purpose plant that produces desalinated ice could offer significant cost savings over combinations of separate desalinators and ice-makers.

The current status of freeze desalination is reviewed, and the important aspects relating to mines are discussed. Some freezing processes that could be suitably modified are described. The possible use of conventional ice-making machines for desalinating mine water is also discussed.

SAMEVATTING

Die tegniese en ekonomiese uitvoerbaarheid van vriesontsouting word oorweeg as 'n tegniek om ys vir die verkoeling van diepmyne te verskaf en tegelykertyd mynwater te ontsout.

Vriesontsouting is nog nie ten volle of kommersieel ontwikkel nie. Vir seewaterdoeleindes bied die metode dalk nie wesenlike voordele bo ander ontsoutmetodes nie, maar vir die unieke gebruik daarvan in die mynbou kan een tweedoelaanleg wat ontsoute ys produseer, aansienlike kostebesparings bo kombinasies van afsonderlike ontsouters en ysmasjiene bied.

Die huidige stand van die ontwikkeling van vriesontsouting word in oënskou geneem, en belangrike aspekte wat met die toepassing van dié proses in die mynbou verband hou, word bespreek. 'n Paar vriesprosesse wat dalk nog wysiging geskik sal wees, word beskryf. Die moontlikheid daarvan om konvensionele ysmasjiene vir die ontsouting van mynwater te bruik, word ook bespreek.

Introduction

The desalination of waters by freezing is a well-known process and relies on the principle that the structure of an individual ice crystal does not accommodate salts. Therefore, during the freezing of a salt solution, salts are rejected by the growing ice crystals. The crystals can be separated from the concentrated solution, which is rejected as brine, and melted to yield pure water.

Several advantages are claimed for freezing over other methods of desalination, including the following.

(i) The quantity of heat to produce 1 kg of clean water from ice is about one-seventh of that needed to make an equivalent amount of water from the condensed vapour of a boiling or distillation process. This is because the latent heat of fusion of ice is 335 kJ/kg and that of vaporization is 2500 kJ/kg. This does not mean, as is sometimes claimed, that freezing is thermodynamically a more efficient process; it means simply that the inevitable thermodynamic losses in heat exchange are minimized.

(ii) Unlike many desalination processes, freeze desalination is virtually insensitive to the salinity and composition of the feed water; a product of low salinity (400 p.p.m. of total dissolved solids or less) can be delivered in virtually all cases. Furthermore, a very high proportion of the feed water can be recovered as clean water.

Despite these advantages, no full-scale commercial freeze desalinator has yet been built; only freeze concentrators have successfully applied the principle. The main reason is that, because of high capital costs, no significant savings in total costs have been anticipated in the production of desalinated water by freezing over other more established methods. In the mining industry, however, a unique situation has arisen in which desalinated ice could be used. This makes freeze desalination an appropriate and, in some instances, possibly the most cost-effective process for mine waters.

The Mining Application

Attention was recently directed to the improvement of the water circulating in mines. In many mines, desalination may be required for one or more of the following purposes:

(i) to reduce the scaling and corrosion of pipes, heat exchangers, and other equipment,

(ii) to reduce the salinity of service water and make it suitable for operating water-powered hydraulic machinery,

(iii) to conserve water by recycling,

(iv) to make all the water piped into a mine safe to drink, and

(v) to reduce the pollution of land and water sources caused by rejected highly saline water.

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The current practice in the cooling of mines is to distribute chilled service water. However, in some deep hot mines it would be advantageous to send ice underground in place of water, and so gain the increased cooling effect of the latent heat of melting ice[1].

The combined needs of any mine can be met by the installation of separate desalination plants and water chillers (or ice-makers) as appropriate. Standard equipment exists, but it appears from current studies by the Chamber of Mines of South Africa Research Organization[2] that a modified form of reverse osmosis process, seeded reverse osmosis (SRO), is better suited generally to the desalination of mine water with its widely varying composition and salinity, than the standard reverse osmosis process or other processes. In some instances, electro-dialysis reversal (EDR) may also be suitable.

Distillation, which is the most widely used desalination process, is not suitable for mines for two main reasons. Firstly, low-cost heat energy is not normally available on mines and, secondly, most distillation processes are limited in their operation by the scaling of heat-transfer surfaces. The vapour-compression distillation processes that do not suffer from scaling have high energy consumptions.

All non-freezing processes add energy to water and increase its temperature, with the result that additional refrigeration capacity is required to produce chilled water or ice. Only freeze desalination removes energy from water, thus reducing its temperature and consequently the refrigeration duty. Furthermore, freeze desalination has the potential to produce desalinated chilled water or ice in a single dual-purpose unit. There is therefore the possibility of developing, or suitably modifying, a freeze desalinator and so effecting significant savings in capital costs over the use of separate plants. The major savings will arise in the production of desalinated ice for the mines that require ice for cooling and also require desalinated water. Ice can be made on the surface, sent underground, and melted for cooling, and the resulting water will be clean.

In principle, any ice-making process is also a potential desalination process. Consideration is currently being given to the development of large-scale conventional ice-making machines for mine cooling. Current commercially available units normally produce up to about 70 t of ice per day but, for the mining application, units of 500 t/d or more would be more suitable. Normally, desalination is not a feature of conventional ice-makers; it is a secondary and often irrelevant effect. However, it is possible, by suitable modifications, to obtain some degree of desalination. Therefore, for the dual-purpose mining application, attention is being given to both ice-makers and freeze desalinators.

Relevant Features of Desalination Processes

Desalination techniques and freezing processes are described in the literature[3], but it is appropriate to review some of the salient features relating to the mining application.

Recovery Ratio

All desalinators should have a blowdown, or reject, stream to dispose of the salt-concentrated brine. The essential features of a desalination process are illustrated schematically in Fig. 1. The three main streams (feed, product, and reject) are shown in addition to an internal recirculation stream. The diagram applies generally to any desalination process and, in a freezing process, the internal method of separating water from a salt solution would be contained in a freezing element.

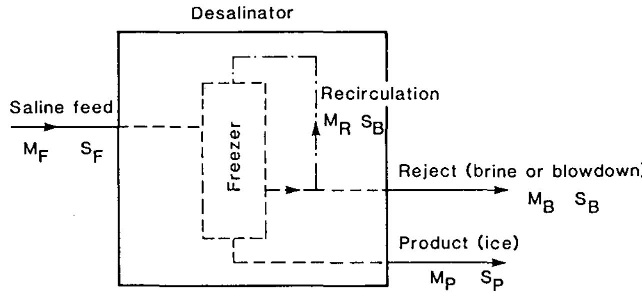

Fig. 1—Schematic diagram of a desalinator

M_F Flowrate of feed, kg/s
M_B Flowrate of reject, kg/s
M_p Flowrate of product, kg/s
M_R Recirculation flowrate, kg/s
S_F Salinity of feed, mg/l or p.p.m. of total dissolved solids
S_B Salinity of reject (and recirculated) liquid, mg/l or p.p.m. of total dissolved solids
S_p Salinity of product, mg/l or p.p.m. of total dissolved solids

One important function of a desalinator is expressed by the recovery ratio, which is the ratio of the product flowrate to the feed flowrate. In the nomenclature of Fig. 1, the recovery ratio is

$$M_p/M_F = S_F/S_p - M_B/M_F \cdot S_B/S_p.$$

Fig. 2 shows a graphical representation of this expression, and illustrates the relationship between recovery ratio and several values of the feed and product salinities. It can be seen that a product of low salinity can be obtained at any recovery ratio, but that the salinity of the brine always increases as the recovery ratio increases.

It is important to note that, for a high recovery ratio, brine is recirculated through the freezer. In effect, the freezer acts as a multi-pass heat exchanger; with each

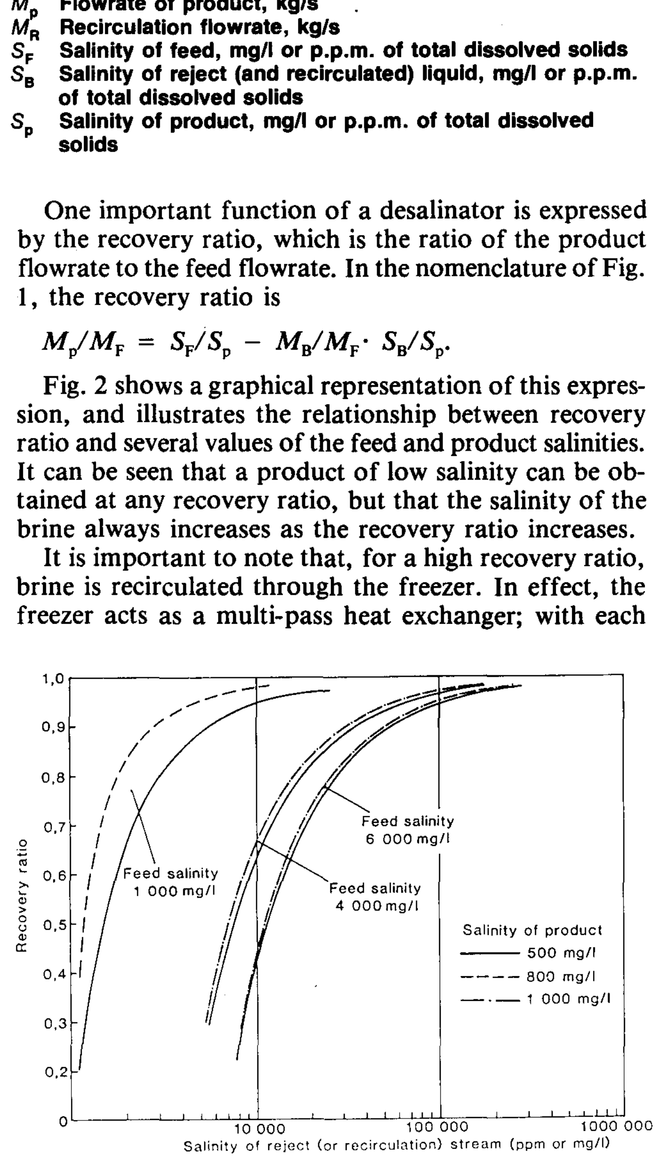

Fig. 2—The relationship between recovery ratio and salinity

pass, more ice is frozen out of the solution. The alternatives, which would generally be more costly, would employ a very large freezing surface area or several freezers in series. The rate of recirculation and the associated pumping energy and costs are set against the cost of providing adequate heat-transfer surface for the same output. Normally, the rate of recirculation will be many times that of the feed flowrate, with the result that the effective salinity of solution passing through the freezer is that of the reject or recirculation stream and not that of the feed.

Ice Formation

It is well known that the equilibrium freezing temperature of a salt solution decreases as its salinity increases. The difference between the equilibrium freezing temperature of pure water (zero salinity, 0°C) and that of a concentrated solution is known as the freezing point depression (FPD).

Mine water contains a variety of salts in varying proportions, and the exact relationship between FPD and salinity is not known. However, as an indication, the values for sea water could be used (Fig. 3). The effective freezing temperature will be even lower in practice than that given by the FPD because a temperature driving force has to be provided for heat transfer and to overcome thermal resistances.

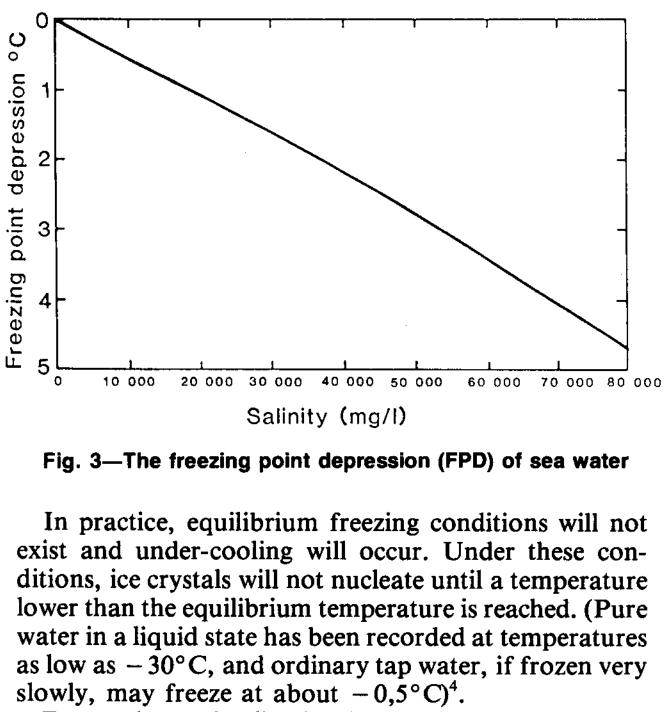

Fig. 3—The freezing point depression (FPD) of sea water

In practice, equilibrium freezing conditions will not exist and under-cooling will occur. Under these conditions, ice crystals will not nucleate until a temperature lower than the equilibrium temperature is reached. (Pure water in a liquid state has been recorded at temperatures as low as −30°C, and ordinary tap water, if frozen very slowly, may freeze at about −0,5°C)[4].

For maximum desalination from a freezing process, the ice ideally should be in the form of individual large crystals. Although ice crystals themselves are pure, salts adhere to the surface of the crystals, and one of the difficulties experienced in freeze desalinators is the economic removal, by washing, of the surface salts. By having suitable shapes and sizes of crystals (preferably spherical), the ratio of the surface area to the volume of ice is minimized, thus easing the washing process. For the continuous production of suitable ice crystals, they should nucleate and grow in the body of a salt solution and not attach themselves to the surface of a tube or plate. In dilute solutions, ice tends to form preferentially on a local surface whereas, in concentrated solutions, crystals tend to form in the body of the solution.

It has been shown[4,5] that the degree of under-cooling influences the nucleation of crystals, their rate of growth, and their eventual shape and size. Another influencing factor is the rate of heat removal. All these factors, in turn, are themselves influenced by the composition and salinity of the solution. Data are available for simple salt solutions and for sea water based on extensive tests, but there are no satisfactory analytical methods for use in the prediction of the properties of complex solutions. No data are available for the range of mine waters encountered, but preliminary tests have indicated trends similar to those given for sea water. For sea water, optimum under-cooling[3,6] is about 0,6°C, and the FPD for a recovery ratio of 0,5 (typical for sea water and corresponding to a reject salinity of about 70 000 p.p.m.) is about −4°C. The crystals produced are of platelet form and have an average dimension of about 150 to 200 μm. Some preliminary tests on mine water have indicated that the best conditions for crystal nucleation and growth to similar sizes occur in a highly concentrated solution, having a salinity of about 100 000 p.p.m. This is significant because it means that, whatever the salinity of the mine feed water (typically 2500 p.p.m.), pre-concentration by recirculation through the freezer is required before the best conditions are achieved for effective crystal nucleation and growth. Therefore, the salinity of mine water is of relatively little consequence.

It is clear that the optimum conditions for desalinated ice-making are a complex combination of many factors. Even to approach the optimum conditions requires careful control of several parameters and, in addition, the slowest possible rate of heat transfer. A slow rate of heat transfer, resulting from small driving forces, will also tend to reduce the energy consumption during ice-making. Experimental freeze desalinators have generally operated under very carefully controlled conditions, and comparisons of specific energy consumption (kilowatt-hours per cubic metre of product water) have shown that freeze desalination is one of the more energy-efficient processes (Table I)[7]. The main reason why the total costs are not significantly lower than those of other desalinators is that, owing to the relatively low rate of ice production, the capital costs are high. However, a moderately carefully controlled freeze desalination process, with adequate washing of the crystals, would probably produce water of a sufficiently low salinity for the mining application in all cases, regardless of the composition of the feed. It is anticipated that water containing about 750 p.p.m. of total dissolved solids would be satisfactory in many cases.

Most published data refer to sea water, and have to be treated with care when applied to mine water because of the important differences between sea water, which has an almost constant composition and salinity (about 80 per cent sodium chloride) and the widely varying constituents of mine waters. For example, if the necessary pre-concentration is 70 000 p.p.m., this corresponds to a recovery ratio of only 0,5 for sea water with a normal

TABLE I
COMPARISON OF THE ENERGY-EFFICIENCIES OF DESALINATION PROCESSES

Form of primary energy	Process	Energy consumption kW·h/m³ Commercial	Demonstrated	Conceptualized
Heat	Distillation	25	15	15
	Freezing	–	27	15
Electrical	Electrodialysis	–	13	9
Mechanical	Distillation*	20	15	10
	Freezing	–	11	8
	Reverse osmosis†	10	7	5

* Mechanical vapour-compression distillation
† Standard process

salinity of 35 000 p.p.m. For mine waters with an initial salinity of 2500 p.p.m., the recovery ratio is over 0,9. Generally, a low recovery ratio is acceptable only if there is ample feed water available, such as from the sea. Furthermore, the large volumes of reject water can easily be disposed of in the sea. In land-based installations, disposal is often a problem, and the reject is a potential pollutant of rivers and other water sources. Moreover, if water is to be conserved, a high recovery ratio of mine water is desirable, if not necessary.

A factor of considerable importance is the presence of scaling salts, notably calcium sulphate (gypsum), which has a low solubility at low temperature. Most mine waters are high in calcium sulphate, and some are saturated. In almost all instances, calcium sulphate will precipitate during freezing. Careful attention is required to ensure that precipitates do not foul heat-transfer surfaces or act as nucleation sites for ice crystals.

Conventional Ice-Makers

Several types of conventional ice-making machines are available commercially[8]. In most cases, ice is made quickly at an economic rate, and it forms as a layer on the surfaces of tubes, plates, or drums. In many respects, this method of ice-making is opposed to the requirements for desalination.

In some ice-making machines, there is often little or no blowdown; all the feed water is frozen, including the salts. A typical case is that of block ice-makers, in which the ice is made in batches in containers (in a manner similar to that in domestic ice-cube makers). All the salts are frozen into the ice, and consequently there is no desalination. In continuous ice-makers, a blowdown can be arranged with little difficulty, and the main factor inhibiting the desalination effect is the entrapment of salts in the ice.

The main features of one common type of continuous ice-maker are illustrated diagrammatically in Fig. 4. Mine feed water is distributed from a header tank to fall vertically down the outside of tubes containing an evaporating refrigerant. Ice forms on the outer surface of the tubes, and the remaining unfrozen water falls to the sump, from where it is pumped back to the header tank for recycling. The recirculated water becomes progressively more concentrated in salts as more ice is formed. In time, with sufficient recirculation, all the water could be frozen, but at some stage the concentrated brine can be rejected. When a layer of ice of sufficient thickness is built up on the tubes, the ice is harvested by the passing of hot refrigerant vapour through the tubes, thereby releasing the ice, which falls onto a grid and is removed. Ice made on the outside of the tubes in this way is known as shell ice. Other common designs of ice-makers[8] produce ice inside tubes (tube ice) or on drums (flake ice).

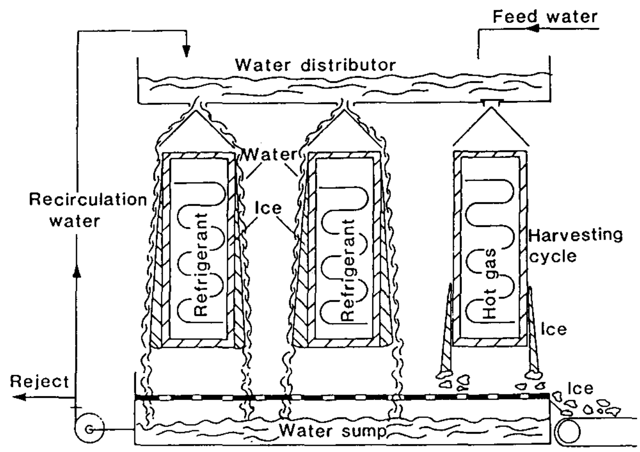

Fig. 4—Schematic arrangement of an ice-making machine

With an arrangement to reject brine, an ice-maker could, in principle, produce desalinated ice. However, the high rate of crystallization, as a result of high temperature-driving forces, tends to favour crystallization on the surface of the tube rather than in the solution. Furthermore, also as a consequence of fast freezing, the crystals agglomerate and salts are trapped between them. This process has been described in detail in the literature[9].

The result is that the ice layer can contain a relatively high proportion of salts from the feed water, even with a suitable rate of blowdown. Tests conducted by the Chamber of Mines Research Organization on some mine waters indicates that, at the normal rates of freezing of commercial ice-makers, the melted ice will probably contain 50 per cent or more of the original salts, depending on the type of salts. In some cases when the feed has a low salinity, the quality of the product water may be acceptable, but in other cases the salinity may be too high. Because of the nature of the freezing process, little improvement in desalination can be expected without a significant reduction in the freezing rate (i.e. the rate of ice production) with conventional designs. One possibility is the use of progressive freezing in a number of units arranged in series. In this way, the driving force in each unit could be reduced and less entrapment of salts may occur, but the equipment costs would be high.

During the formation of ice, the heat-transfer process is indirect because of the metal interface between the refrigerant and the water. There are significant resistances to heat transfer in addition to that caused by the tube itself. The ice layer itself represents a resistance, which increases as the thickness of the ice increases, and scaling, resulting from the precipitation of salts, also constitutes a resistance. The result of the combined resistances is to cause the evaporating temperature of the refrigerant to be lowered and to increase the duty of the refrigeration system. There is a corresponding increase in energy input and a reduction in the overall efficiency of the process. Further energy penalties are incurred in the harvesting of the ice.

However, notwithstanding these effects and also the relatively high salinity, the ice has a high cooling potential. Normally, it is in the form of fragments containing little surface water, and in some cases it can be subcooled. The full latent heat is therefore available for cooling.

Research is continuing, in collaboration with manufacturers of ice-makers, with the aim of developing larger units with an improved desalination effect. However, an alternative ice-making process may be more effective in producing desalinated ice of low salinity.

Slurry ice-makers produce ice as crystals in the body of the water, and therefore inherently have a greater potential for desalination. No attempt is normally made to wash the crystals, and a washer would have to be added to the process. This possibility is being investigated.

The process of ice-making in slurry ice-makers is similar to that in freeze desalinators, which are described below.

Freeze Desalinators

Normally a freeze desalinator produces clean water, not ice; modifications are required to produce desalinated ice, which are described later. The essential features of a normal freeze desalination process to produce desalinated water are described by reference to Fig. 5.

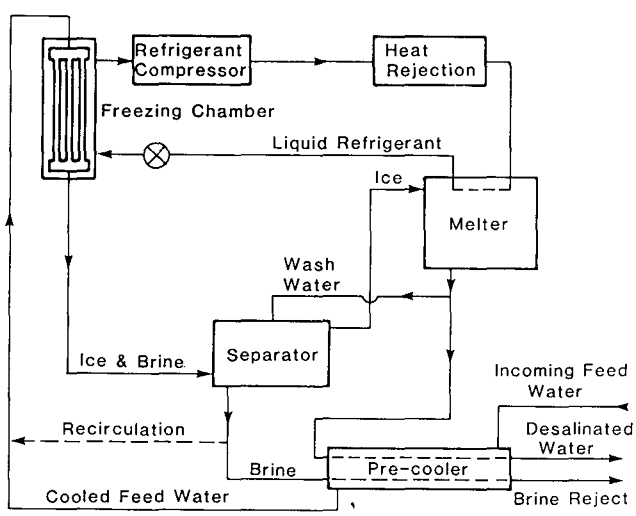

Fig. 5—The indirect freeze desalination process (after Spiegler and Laird[3])

Saline feed water first passes through a pre-cooler and enters the freezer unit, where it flows downwards inside tubes and is cooled to the freezing point by a refrigerant evaporating on the outside of the tubes. Ice crystals form in the body of the flowing solution, and a slurry comprising ice crystals and concentrated brine leaves the freezer and is pumped to a separation unit. In the separation unit, the ice is separated from the brine and is washed. The brine is recycled to the freezer and eventually is rejected via the pre-cooler.

The washed ice is melted in the melting unit by heat, which is rejected by the condensing refrigerant and is discharged via the pre-cooler. The wash water is provided by some of the clean, melted ice (typically 5 per cent).

An additional heat-rejection cooler is needed in the refrigerant circuit. This is because the melting ice does not absorb sufficient heat to condense all the refrigerant. In many cases, the additional cooler will be the evaporator of an auxiliary refrigeration system.

The most critical processes occur in the freezer and in the washer. In the freezer, the process of heat transfer is indirect because of the metal interface between the water and the refrigerant. Although there are some resistances to heat transfer, these are significantly less than in an ice-maker, and are not generally too severe as long as ice or precipitate salts do not scale the surface of the tube. There are several methods to prevent surface fouling by precipitate salts, including the use of mechanical scrapers and special treatment of the tubes. The prevention of ice formation on the surfaces of the tubes is essential. In addition to the factors relating to optimum crystal growth mentioned earlier, the velocity of flow through the tubes and the degree of turbulence or agitation are also important. In general, and because of the complex nature of a multi-salt solution, the optimum conditions must be determined by tests, and one aim of the current research is to determine these conditions for mine waters.

In the washer, it is necessary, for minimum energy consumption and maximum cost-effectiveness, that the surface salts should be removed with the minimum of wash water. If the crystals are large, uniform, and spherical, the distribution of wash water is even, and the washing is most effective. Most washers are similar in design and are described in the literature[3].

Several alternative designs of freezer exist[3]. The principal aim of most of these designs is to improve the efficiency of the process by employing direct-contact heat transfer. The methods include the direct mixing of an immiscible refrigerant with the water, and direct evaporation under vacuum. In principle, direct-contact freezing methods are preferable because very high heat-transfer coefficients can be achieved, but in practice additional complications arise in the refrigeration systems. The merit of the indirect process is that a standard refrigeration system can be used.

There are also several alternative designs of plants[3]. Some incorporate the freezer, separator, and melter in a single vessel; others employ absorption refrigeration systems. None of these arrangements has yet been developed fully or commercially as a freeze desalinator, but indirect freezing processes are used successfully for the freeze concentration of fruit juices and liquors.

Freeze concentration is a process similar to freeze desalination. One basic difference is that the product and reject streams are reversed; in concentrators the concentrated 'brine' is the product. Much attention has been given to the optimum conditions for nucleation and crystal growth in fruit juices, and the results of this work can be applied with advantage to mine waters. One reason for the cost-effectiveness of freeze concentrators is that the product has a high economic value, and this often justifies the relatively high capital cost of the equipment.

(Another reason is that, with freeze concentrators, little or no product flavour is lost by the removal of volatile elements such as occurs in distillation processes.)

Modified Freeze Desalinators

After a review had been made of different freeze-desalination processes in various stages of development that could be suitable for the mining application, it was concluded that the indirect freezing process is preferable at this stage. It is the simplest and is in the most advanced stage of development. Eventually, however, one of the direct processes may be preferable because of its potentially higher efficiency.

Preliminary tests have already been conducted on one indirect process. This was designed for the desalination of sea water, and short tests with three simulated mine waters indicated that no great difficulties should be experienced in the modification of the process to deliver desalinated chilled water or ice. However, the tests showed that two aspects require further examination. The first concerns the possible deposition in time of salts and ice on the surface of the tubes at relatively high rates of ice production, which would impair heat transfer. The second concerns the removal of precipitate salts. The removal of precipitates is not normally a feature of freeze desalination processes for sea water because scaling salts are not present in such high concentrations at normal recovery ratios.

Desalinated Ice

By reference to the basic flow diagram of an indirect process in Fig. 5, two modifications are necessary for the production of desalinated ice. First, the pre-cooler must be replaced by a pre-cooling water chiller. Alternatively, additional heat could be removed in the freezer, but it is not desirable to change the critical operating conditions and heat flux in the freezer at this stage. Second, a larger cooler has to be installed to condense the refrigerant; only sufficient ice would be melted to wash the crystals. These are relatively minor modifications, although they will affect the energy-efficiency of the process. It is clearly more efficient to condense the refrigerant by melting ice than it is to employ a conventional heat-rejection system.

Normally, the ice that is delivered from the washer to the melter consists of a slurry having a maximum ice mass fraction of about 50 per cent. For the economic use of ice for the cooling of mines, an ice mass fraction of 70 per cent or more would be preferred in many cases (this depends upon the conditions and layouts of the mine concerned). Some re-design may therefore be necessary.

The salinity of the ice-water slurry will be about 400 p.p.m. In many instances, this will be too high a quality for mining applications, and it is expected that, in practice, only part of the water would be desalinated and this would be mixed with mine water to give a mixture of suitable quality.

Desalinated Chilled Water

To produce desalinated chilled water instead of desalinated ice, only the pre-cooler has to be replaced; the rest of the system would remain as at present.

Cost Comparisons

Preliminary cost comparisons have been made between alternative methods for the production of both desalinated chilled water and desalinated ice. There is large uncertainty in the costs because no large-scale plants designed specifically for mines have yet been built or costed.

However, based on the research to date, it is expected that, for the production of desalinated chilled water, there will be little difference in the cost per cubic metre of product water between an SRO unit followed by a water chiller and a modified freeze desalinator. For the production of desalinated ice, it is expected that the cost per ton of ice could be about 25 per cent cheaper from a modified freeze desalinator than from an SRO unit followed by a conventional ice-maker.

Costs cannot be given more accurately at this stage, and no final judgement can be made until better figures are available.

Conclusions

There is expected to be a need on some mines for the production of desalinated chilled water or desalinated ice. From an examination of conventional ice-makers for their ability to produce desalinated ice, it is concluded that a relatively small desalination effect is obtainable at economic freezing rates. From a similar examination of partially developed freeze desalination processes, it is concluded that suitable modifications could be made so that the product is chilled desalinated water or ice of low salinity.

Preliminary cost comparisons indicate that a modified freeze desalinator is probably the most cost-effective way of producing desalinated ice.

Acknowledgements

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