天然气水合物及相关新技术研究进展*

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胡玉峰.天然气水合物及相关新技术研究进展.天然气工业,2001;21(5):84～86

摘　要　二十一世纪潜在新能源天然气水合物的开发利用、天然气水合物在环保、化工、航天和生物工程领域的应用研究、以及基于天然气水合物的各种新技术的研制开发是现今的研究热点和发展方向。文章介绍天然气水合物及有关新技术的研究现状,包括其作为潜在新能源的巨大优势,在环境保护、生物工程和航天领域的应用、对油气工业的影响,以及基于天然气水合物的各种新技术的研制开发。文章还简析了以上诸方面潜在的技术优势和广阔的应用前景、各项研究的技术关键、难点和尚存在问题。

主题词　天然气　水合物　替代能源　技术　开发　环境保护　研究

二十一世纪潜在的巨大新能源

天然气水合物是天然气存在的一种类型,可视为高度压缩的天然气。它由甲烷和水在一定的温度和压力条件下笼合而成。每立方米天然气水合物分解释放160～180立方米天然气。国外现已探明的存于海底沉积层和大陆冻土带地层中的天然气水合物储量已相当于全球非再生能源(煤、石油、天然气、油页岩等)储量的2.84倍左右[1]。

作为一种潜在的巨大洁净新能源,80年代以来,俄罗斯、美国、加拿大、挪威、英国、日本和印度都相继开展了对其的勘探工作,但迄今尚无开采天然气水合物特别有效的方法。已试用的方法包括注入热水、降低储层压力、注入抑制剂、采用微波技术等。美国能源部对开采天然气水合物信心十足,最近宣称将在10～15年内解决天然气水合物开采问题。

与全球环境保护的关系

CH_4的温室效应是CO_2的21倍(大气中CH_4的浓度仅为CO_2的5‰,但对温室效应的贡献却占15%),属高强度的温室效应气体。目前大气中的CH_4正以近于1%的速度增长[2],因此国内外已经开始重视天然气水合物对全球生态环境可能造成的影响。比如,若全球变暖导致某些地区水合物分解,则大量CH_4的释放将使温室效应更为加剧,而温室效应的加剧又将进一步加速水合物的分解,这种恶性循环的后果不堪设想。迄今,已提出许多理论模型试图按目前温室效应加剧的速度估算使天然气水合物分解所需的时间,初步结果为:海底水合物将在今后1 000年内保持稳定,大陆冻土带地层中的天然气水合物将在今后100年内开始分解。所幸的是,后者的储量仅为天然气水合物总储量的1%[3],人类还有时间研究解决这一问题。此外,在某些情况下,由于水合物的生成和分解而引起的海上油气井自喷还会造成严重的海洋污染。

另一方面,利用水合物技术是目前人类正在研究的解决温室效应问题的途径之一。其基本原理是:利用CO_2易于生成水合物的原理,将大气中的CO_2分离并以水合物形式储存于海底深处(通常温度介于2～4℃,适合生成CO_2水合物,且CO_2水合物的比重大于海水,因此便于储存)。此外,美国和日本均在研究将工业废气中的CO_2生成水合物并存储在海底的技术,1997年还专门在比利时组织召开了第一届水合物技术与环境保护国际会议。值得一提的是,Ohgaki等在研究CO_2和CH_4混合气在280 K条件下的气—液—固(水合物)三相平衡时发现,

*本文系石油大学校基金资助项目内容(ZX9903)。

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水合物相中的 CH_4 可有选择性地被 CO_2 置换。这无疑预示着人类可将解决温室效应和开发天然气水合物相结合的可能性:用大气中的 CO_2 置换天然气水合物中的 CH_4。

此外,基于水合物的污水处理技术也日益受到重视。世界专利 WO8910892 介绍了利用水合物技术处理油田废水的方法:利用气体和油田废水中的水生成水合物,将沉积下来的水合物固体分离后,再进行分解,达到纯化废水的目的。而 Ngan 等则利用 C_3H_8 水合物法处理造纸厂的废水;Yoon 等研究了利用 CO_2 水合物法处理酚水溶液的可行性。

基于水合物的新技术开发

除去能源、环保领域外,如何通过水合物生成机制开发一些和工业、民用甚至航天有关的新技术近年来已引起广泛重视。现将若干研究方向作一简单介绍。

1. 天然气的固态输送和储藏

当天然气需越洋作长距离输送时通常采用低温液化航运输送。这种输送方式成本高,安全性差。经研究,若将天然气先转化为水合物,再在固态下航运输送可达到经济和安全的目的。据报道挪威已成功地开发了在 - 15 ℃和常压下以水合物状态输送天然气的技术,成本较低温(- 160 ℃)液化输送约减少 24 %。

由于天然气水合物可视为高度压缩的天然气,因此当有大量天然气需要储存时也可使之转化为水合物状态储存于地下。显然,对于其他可形成水合物的气体(如采油注气生产中大量使用的 CO_2)也可考虑通过水合物方式进行输送或储存。

2. 天然气水合物作为车用燃料

随着石油资源的日见枯竭及城市污染的日益严重,国内外都在试行推广使用天然气汽车。目前天然气汽车使用的燃料大多是压缩天然气(一般需压缩至 20.0 MPa)。使用压缩天然气的缺点是存储压力高和行程短。为克服上述缺点,美国已在试验将天然气水合物(其平衡压力仅为 4.0 MPa)作为车用燃料。所涉及的关键技术将是如何使水合物快速气化以满足内燃机系统的需要。天然气水合物具有高浓度、高储量的特点,每单位体积可储存标准状态下 164 倍体积的天然气,因此行驶距离长,比压缩天然气汽车、液化天然气汽车和活性炭吸附天然气汽车更具优势。

3. 基于生成天然气水合物的新型分离技术

水合物的生成具有选择性,其晶体中只包含主体和客体分子,且二者在水合物相和非水合物相中的组成不同。据此,可进行以下分离:

(1)海水淡化技术[4]

由于海水中溶解的盐类不能形成水合物,如向其中注入某种气体(如 CO_2)使之与水生成水合物,然后进行固液分离并使水合物分解即可淡化海水。此项技术始见于 1942 年,而到 1960 年以后已形成了许多专利并在中试装置上获得成功,其优点是设备简单、能耗低。但迄今仍未大规模工业化,原因是生成水合物时伴随着机械夹带使人们较难得到高纯的饮用水,这一问题目前正在研究解决之中。

以上方法已被用于油气田和造纸厂的废水处理(前者还可同时回收油气)。世界专利 WO8910892 介绍了利用水合物技术处理油田废水、回收油气的方法。Ngan 等利用 C_3H_8 生成水合物从造纸废水和质量分数为 2.5 %的 NaCl 溶液中回收水,回收得到的水中盐含量降低了 31 %,在此分离过程中若用液态 C_3H_8 进行冲洗可改善分离效果。Yoon 等研究了利用 CO_2 生成水合物处理酚水溶液的可行性。加拿大哥伦比亚大学化工系的 Englezos 等通过注入 C_3H_8 生成水合物处理造纸厂废水,初步研究结果使水中盐浓度和废物浓度分别降低 23 %和 26 %。

(2)有机水溶液的浓缩

若将水合物生成剂加入稀的水溶液并使与水生成水合物,然后进行固液分离,可达到浓缩水溶液的目的。

Huang 等的研究结果表明,在碳水化合物、蛋白质或类脂化合物的含水体系中,CH_3Br 和 CH_3F 极易生成水合物,因而可作为水合物生成剂用于提浓苹果汁、橙汁和土豆汁。该法可除去其中 80 %的水分。美国专利 US 4678583 介绍了下列稀水溶液提浓技术:①在 12 ℃,6.5 MPa 利用乙烯水合物提浓质量分数为 0.082 %的丁醇水溶液;②在 4 ℃,5.5 MPa 利用 CO_2 水合物提浓质量分数为 4 %的丙烯酸水溶液;③在 4 ℃,利用 CCl_3F 水合物提浓丁醇水溶液。Heist Engineering 公司在甜菜生产中利用水合物法代替能耗很大的蒸发法。而对诸如咖啡抽提物、蔗糖水溶液等不宜高温蒸发或粘度较高的溶液,可用环氧乙烷作为水合物生成剂加以提浓[5]。该法的另一突出优点是可在冰点以上实现提浓,比传统使用的冷冻浓缩法或蒸发提浓法具有十分明显的节能优势,因此在制糖工业等领域具有十分广阔的应用前景。

(3)气体混合物的分离

气体混合物中能生成水合物的气体是分子量介于 Ne 和 C_4H_{10} 之间的非极性气体和少数极性气体(CO_2 和 H_2S 等),且在一定操作温度下不同气体生成水合物所需的压力通常差别较大,比如,0 ℃时 N_2、CH_4 和 C_2H_6 水合物的生成压力分别为 14.3、2.56和 1.01 MPa。据此,可通过控制操作温度和压力,将给定操作条件下可生成水合物的气体从气体混合物中分离出来。

已有许多关于水合物分离技术的专利和论文发表。Dorsett 将脱水、气体露点控制及强化冷凝过程集中于水合物的生成和分解过程中,并发展了一种低温抽提(LTX)技术。美国的 Bechtel 公司开发了一种从煤燃烧的废气中分离 CO_2 的新技术。首先利用高压 CO_2 使水形成能包容外来 CO_2 分子的水分子簇,然后将其注入废气流中,在较高压力和冰点附近形成 CO_2 水合物,从而把不能生成水合物的氢气从废气中分离出来并用于燃烧发电;水合物则被输送到另一容器中,通过加热或降压释放出 CO_2,水则循环利用。美国能源部类似的研究结果表明,对以煤为燃料的发电厂排放的废气而言,CO_2 的分离效率可达 86 %,氢气的回收率则高达 99.8 %。前苏联专利 SU1648527 介绍了利用水合物分离气体的技术:在 5 ℃,5.0 MPa 下,使混合气体通过含水合物促进剂的水溶液,其中乙烯或其它轻质气体因可生成水合物而被分离。Elliot 通过控制操作条件,利用水溶液吸收特定的气体组分,实现了从天然气中分离特定的烃类组分的目的。

(4)近临界和超临界萃取

Wilson 等在用乙烯萃取 L-苯基丙氨酸溶液中的正丁醇时发现,当体系温度降低到乙烯生成水合物时,水溶液中 L-苯基丙氨酸的浓度和乙烯中正丁醇的浓度都显著地提高了;在一定时间范围内,二者增浓的比例接近,但不相等,其原因有三:混合不完全,正丁醇的分配系数随浓度发生变化,以及 L-苯基丙氨酸或正丁醇被水合物吸附。Wilson 等的结论是:水合物的生成可显著提高近临界和超临界萃取过程的有效分配系数,且增幅介于 1.7～6.4 倍之间;水合物的生成还可增加萃取过程的选择性。这使得人们能够在减少设备投资和能量消耗的同时提高溶剂萃取效率,但随之而来的问题是,水合物相的传质和传热效率较低,将延缓热力学平衡速率;水合物晶体的生长速度较慢,将直接影响萃取过程达到平衡的速率。解决问题的办法是加大溶剂和水溶液的进料速率并使水合物尽量分散,同时添加适量表面活性剂并辅以超声波乳化以提高水合物生成的动力学速率。

(5)用作航天自动制冷饮料

随着航天事业的迅速发展,宇航员(特别是长期在空间站中生活的宇航员)在空间生活中所需的冷饮由于宇航站能源的严格限制难以供应。而利用水合物技术可以生产出无需外界制冷的冷饮。其基本原理是在饮料瓶(能耐一定压力)中置入一定量由无害气体(如 CO_2)形成的水合物,当启开饮料瓶时由于压力降低,水合物分解吸热而自动制冷。

天然气水合物用于生物工程和新材料领域

Rao 等经研究发现气体水合物的生成可以促进高分子溶液中酶的活性。Lund 等也发现气体水合物对食物和生物体内的酶几乎无任何负面影响。Hull 和 Fennema 则发现,若在结晶物生成之前使环氧乙烷扩散到细胞内,则水合物可在细胞体内生成。Philips 等利用水合物法从生化溶液中提取蛋白质。此外,在发酵过程和制药过程中都可以利用水合物法进行分离,比如,John 利用水合物法从发酵物中提取蛋白质和生物制品。水合物法还被用于进行生物模拟晶和生物酶活性控制、进行半导体纳米材料的开发和其它高级材料特别是微束半导体胶质的制备等。

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(收稿日期　2001 - 02 - 14　编辑　申红涛)

Oil Field). *NATUR. GAS IND.* v. 21 ,no. 5 ,pp. 77～79 ,9/ 25/ 2001. (ISSN1000 - 0976 ; **In Chinese)**

ABSTRACT : In order to handle the contradiction between the input and output in the low-permeability oil and gas reservoir development and to meet the needs of the rational production rate and stable production period to obtain maximum economic benefits ,the bulk reformation technique is applied more and more widely in every oil and gas field. In this paper , by comprehensively applying oil reservoir engineering method ,numerical simulation theory , seepage flow mechanics theory , oil production engineering and numerical calculation method ,etc. , starting from the bulk reformation of the tract and in view of the effect of both the low-velocity non-Darcy seepage flow in the low-pearmeability tight gas reservoirs and the high-velocity non-Darcy seepage flow in the man-made fractures ,a new and more perfect bulk fracturing simulation mathematical model for low-permeability tight gas reservoirs is set up for the first time ,a numerical model is derived and the bulk fracturing simulation software for low-permeability tight gas reservoirs is drawn up ,providing a powerful tool for drawing up the bulk fracturing reformation plan for low-permeability tight gas reservoirs.

SUBJECT HEADINGS : Low-permeability oil and gas reservoir , fracture (rock) , Fracturing , Numerical simulation , Performance ,Design ,Model

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A STUDY OF DEVELOPMENT TECHNIQUE OF LAMADIAN UNDERGROUND NATURAL GAS STORAGE IN DAQING

Sha Zonglun ,Fang Lingyun ,Fang Liang and Shu Ping (Daqing Oil Field Co. Ltd.). *NATUR. GAS IND.* v. 21 ,no. 5 ,pp. 80～83 ,9/ 25/ 2001. (ISSN1000 - 0976 ; **In Chinese)**

ABSTRACT : The Lamadian underground natural gas storage in Daqing was constructed on the basis of the gas cap of Lamadian bedded sandstone oil field in Daqing and is one of the earliest one that was put into use in China. Through the practice of gas injection and recovery for over 20 years ,it is indicated that the natural gas storage and recovery by utilizing underground gas storage is the most efficient measure for the rational utilization of natural gas resource , which not only effectively solves the problem of non-equilibrium gas consumption due to the difference between summer and winter in Daqing region and due to petrochemical plant 's production being held up for reparing equipments ,but also effectively protects the environment. In this paper , the development course of the Lamadian underground gas storage in Daqing and the main way of doing in every stage are reviewed and a set of the main development techniques for the gas storage ,such as the design of the gas storage , the volume calculation method for the gas injection and recovery system ,the monitoring and regulating technique for the dynamic system ,the adjusting technique for forming a complete surface technology ,the dynamic analysis technique and the management method ,etc. are expounded ,having a greater technic and econmic value.

SUBJECT HEADINGS : Daqing oil field ,Lamadian ,Underground gas storage , Dseign , Development , Technique , Management , Economic benefit

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PROGERSS IN STUDY OF NATURAL GAS HYDRATE AND RELATED NEW TECHNIQUES

Hu Yufeng (Key Research Laboratory of Oil and Gas Reservoir Fluid Phase State , China National Petroleum Corporation ,University of Petroleum ,Beijing). *NATUR. GAS IND.* v. 21 ,no. 5 ,pp. 84～86 , 9/ 25/ 2001. (ISSN1000 - 0976 ; **In Chinese)**

ABSTRACT : The development and utilization of the natural gas hydrate —a potential new energy source in the 21th Century ,the Study of the application of natural gas hydrate to the fields of environmental protection ,chemical engineering , spaceflight and bioengineering as well as the research and development of the various new techniques based on gas hydrate formation are the research hotpoint and developing direction at prestent. In this paper ,the current research situation of natural gas hydrate and related new techniques (including the great advantages as a potential new energy source ,its being applied to the environmental protection , bioengineering and spaceflight) ,

the effect on oil and gas industry and the research and development of the various new techniques based on gas hydrate formation ,etc. ,are presented and the potential advantages of above-mentioned techniques and their wide application prospects ,the key technique and difficulty in the research works as well as the existent problems are briefly expounded also.

SUBJECT HEADINGS: Natural gas , Hydrate , Substitute energy , Technique ,Development , Environmental protechion , Research

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CURRENT RESEARCH SITUATION OF THE SAFETY IN THE STORAGE AND TRANSPORTATION OF COMBUSTIBLE LIQUIFIED GASES

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ABSTRACT: For the liquified gases to maintain their liquid state ,it is necessary to depend on high pressure and low temperature ,which brings a safety problem more severe than conventional fluids or gases. In this paper ,the existing achievements in the research on the safety in the storage and transportation of liquified gases in the world are reviewed , many safety problems existed in the storage and transportation of combustible gases (LPG and LNG, etc.) are analyzed and the progress and achievements in the research on the vessel heat effect before it is broken ,the boiling liquid expansion vapour explosion ,the diffusion of burnt gas in air and the liquified gases combustion ,etc. are emphatically introduced , and based on which , the safety measures in the storage and transportation of combustible gases are presented also.

SUBJECT HEADINGS: Liquified Petroleum gas , Liquified natural gas , Storage , Transportation , Research , Safety

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THE DESIGN CHARACTERISTICS OF THE ELECTRICAL INSTALLATION IN UPSTREAM SURFACE CONSTRUCTION OF WEST-TO-EAST GAS TRANSMISSION PROJECT AND THEIR CORRESPONDING MEASURES

Zheng Shitong , Guan Yue and Yang Yang (Sichuan Petroleum Survey and Design Research Institute). *NATUR. GAS IND*. v. 21 , no. 5 , pp. 92～96 ,9/ 25/ 2001. (ISSN1000 - 0976 ; **In Chinese)**

ABSTRACT: As a commodity , the electric power requires its production and consumption to have a very good continuity and a strict equilibrium between the supply and demand ,but the electricity supply and distribution network is one of the most important infrastructures for all modern industrial enterprises. In this paper ,from the point of view of system engineering ,the design thought of electricity supply source , electricity-supply network and installations and electricity-distribution network and facilities in the Talimu gas field —the upstream fountainhead of the west-to-east gas transmission project and at the starting point of the long-distance pipeline in the large-scale development of the west region of China is overall introduced ,of which , the countermeasures adopted in the determination of electric load grade and the reliability design of the supply and distribution system assorted with the deliverability and its installations are emphatically presented in view of the special surroungdings of Xinjiang region. The optimization of electricity supply and distribution network and the concrete measures for selecting ripe technique and products is presented also.

SUBJECT HEADINGS: Gas transmission , Surface engineering , Electric equipment , Design

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