

文章编号:1000-5870(2002)02-0079-03

从炼厂酸性气中回收氢气和硫磺的实验研究

刘相, 李发永, 曹作刚, 张海鹏, 李阳初

(石油大学化学化工学院, 山东东营 257061)

摘要:利用氧化还原反应和电解反应构成的双反应工艺,对炼油厂含硫化氢的酸性气进行处理,回收氢气和硫磺。考察了液相流量、液相中 Fe^{3+} 的浓度及气相流量对硫化氢吸收传质速率的影响,并对双反应工艺的稳定运转进行了实验验证。实验结果表明,该工艺过程可行,在适宜的操作条件下,硫化氢的吸收率可达 99.9% 以上。

关键词:硫化氢; 氢气; 硫磺; 处理; 酸性气; 炼油厂; 双反应工艺

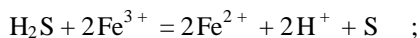
中图分类号: X 742.013 **文献标识码:** A

引言

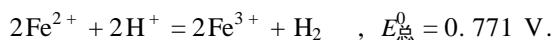
炼厂酸性气是石油加工过程中伴生的副产物,其主要成分为硫化氢。目前,处理酸性气的主要方法是采用克劳斯工艺^[1-3]。然而,传统的克劳斯工艺存在以下缺点:设备的投资费用大;在高温下操作, $\text{H}_2\text{S}/\text{SO}_2$ 的比例严格控制在 2:1 左右,实现起来极端困难;经克劳斯工艺后释放出的尾气中硫含量较高,很难符合严格的环保法规,为了达到环保要求,须增加更多的克劳斯段或采用费用很高的尾气净化工艺;克劳斯工艺只回收了硫化氢中的硫,而将大量的氢转化成了水,虽然由此产生的热能可以补偿部分的资源损失,但大量具有应用价值的氢气被消耗,资源的利用率不高^[4]。硫化氢的电化学分解法,可以将硫化氢分解为氢气和硫磺,不仅能够回收硫,而且能够同时回收氢,引起了国内外工业界及学术界的关注^[5-8]。

1 实验原理

采用双反应工艺处理硫化氢制取硫磺及氢气的化学原理是利用氧化还原反应使硫化氢氧化得到固体硫磺和 H^+ ,再进行电解反应将 H^+ 还原得到氢气。氧化还原反应和电解反应分别在反应器和电解池中进行,氧化还原反应的反应式为



电解反应的反应式为



2 吸收反应实验及影响因素

2.1 实验流程

为了探索适宜的操作条件,首先对硫化氢吸收反应(传质过程)进行实验研究,联合运转实验流程见图 1。

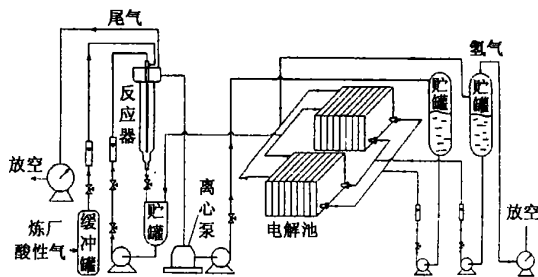


图 1 联合运转实验流程图

先配制一定浓度的 FeCl_3 溶液,放入反应器贮罐中,恒温后通入含硫化氢的炼厂酸性气。用质量流量计和湿式气体流量计分别测定炼厂酸性气和尾气的体积流量,用气相色谱仪分析炼厂酸性气和尾气中硫化氢的浓度,从而计算出硫化氢的体积传质系数。其计算公式为

$$K_y a = \frac{q_1 y_1 - q_2 y_2}{V_{\text{液}} V_{m,0}}$$

式中, $K_y a$ 为体积传质系数, $\text{kmol}/(\text{h} \cdot \text{m}^3)$; q_1, q_2 分别为炼厂酸性气、尾气的体积流量, L/h ; y_1, y_2 分别为炼厂酸性气、尾气中硫化氢的摩尔分数; $V_{\text{液}}$ 为反应液的体积, L ; $V_{m,0}$ 为理想气体的摩尔体积,

收稿日期:2001-10-10

基金项目:“九五”国家科技部重点科技攻关课题(96-A-17-07-01)

作者简介:刘相(1969-),男(汉族),山东莒南人,讲师,硕士,从事化学工程研究。

$V_{m,0} = 22.4 \text{ m}^3/\text{kmol}$ 。

2.2 影响因素

2.2.1 液相流量

保持气相流量不变,考察液相流量对体积传质系数的影响,结果见图2。由图2可见,在气相流量一定的条件下,硫化氢的体积传质系数并不随液相流量的变化而变化,基本为一常数。因此,在一定的液相流量下,增大液相流量并不能显著地提高硫化氢的吸收效率。这是因为硫化氢的吸收过程是一个快速的化学反应过程,受气膜控制,因此增大液相流量对传质过程的影响不大。由此可知,操作过程可以在较小的液相流量下进行,这样既可以满足传质要求,又可以降低液相的动力消耗,节约操作费用。

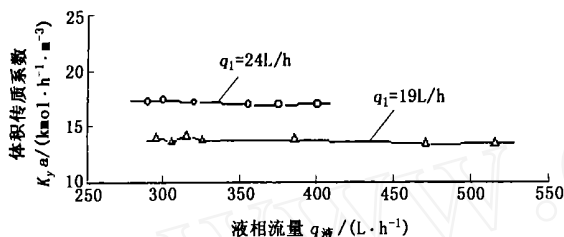


图2 硫化氢体积传质系数与液相流量的关系

2.2.2 Fe³⁺浓度

保持气相流量和液相流量不变,每隔1h从反应贮罐中取液体样,分析其中Fe³⁺的浓度。硫化氢的体积传质系数与Fe³⁺浓度的关系见图3。

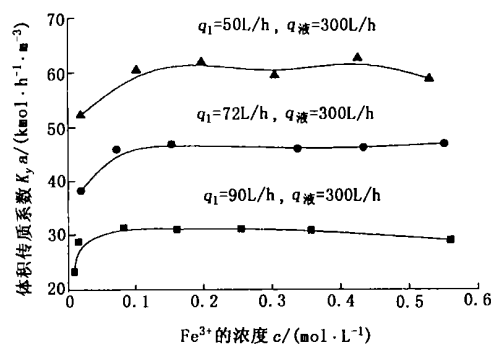


图3 硫化氢体积传质系数与Fe³⁺浓度的关系

从图3可以看出,当Fe³⁺的浓度大于0.1 mol/L时,硫化氢的体积传质系数不随Fe³⁺浓度的变化而变化,基本为一常数;而当Fe³⁺的浓度小于0.1 mol/L时,硫化氢的体积传质系数则随Fe³⁺浓度的降低而降低。这是因为当Fe³⁺的浓度较高(大于某一临界值)时,硫化氢的吸收是一个化学吸收过程,该过程主要由气膜控制,因此Fe³⁺的浓度对其影响

不大;而当Fe³⁺的浓度较低时,由于没有足够的Fe³⁺参与硫化氢的吸收反应,其化学吸收速度会大大减小。因此,为了保证吸收效果,Fe³⁺的浓度不能低于临界值,而应保持在稍高于其临界值的范围内,以满足传质要求。

2.2.3 气相流量

保持其他条件不变,改变气相流量,考察它对硫化氢体积传质系数的影响,结果见图4。可见,在实验操作范围内,硫化氢体积传质系数随气相流量的增大而增大,二者呈明显的直线关系。这是因为气相流量的增大,使得液相中硫化氢的气含率增大,从而增大了气、液两相的传质面积,这就使硫化氢的体积传质系数相应增大。

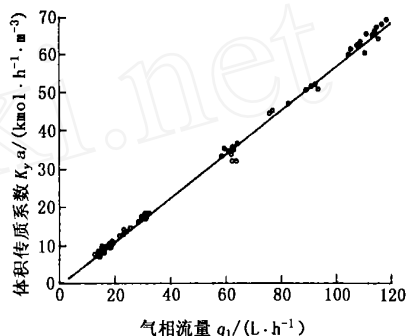
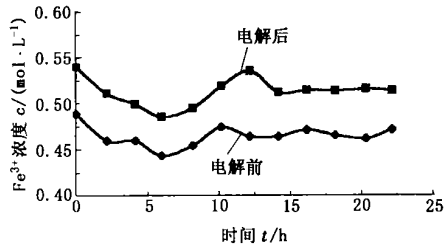


图4 硫化氢体积传质系数与气相流量的关系

3 联合运转实验结果

吸收反应和电解反应能否稳定联合运转,关键在于硫化氢的吸收率、氢气的产率及吸收液中Fe³⁺的浓度是否随运转时间的变化而发生变化。维持炼厂酸性气(硫化氢的含量95%~98%)的进气流量在90~100 L/h,通过24h的连续运转实验发现,硫化氢的吸收率均大于99.9%,氢气析出速度为80~100 L/h,尾气中硫化氢含量约为0.1%,每标准立方米的制氢电耗为2.6 kW·h,吸收液中Fe³⁺的浓度随时间的变化见图5。

从以上实验数据及图5可知,硫化氢的吸收速度和电解制氢速度都保持在80~100 L/h,吸收的硫化氢气体经电解反应生成了同体积的氢气,而且反应液中Fe³⁺的浓度在电解前、后随时间的延长几乎不发生变化,硫化氢的吸收率一直保持在99.9%以上。由此可见,吸收反应和电解反应能够稳定联合运转,将炼厂酸性气中的硫化氢转变为氢气和硫磺。

图 5 电解前、后 Fe^{3+} 浓度随时间的变化

4 结 论

(1) 采用间接电解法从炼厂酸性气中同时回收氢气和硫磺的工艺装置能够稳定运转。硫化氢吸收率较高,达到 99.9% 以上。

(2) 在实验操作范围内,当 Fe^{3+} 的浓度大于 0.1 mol/L 时,硫化氢传质速率与 Fe^{3+} 的浓度无关而与气相流量的大小成正比;在保证液相流量能将硫化氢气体带入吸收反应器的条件下,液相流量的增大对硫化氢的传质速率影响不大,应尽可能采用较小的液相流量,以节约能耗。

参考文献:

- [1] 俞英,等. 硫化氢间接电解制取氢气和硫磺方法的研究[J]. 石油与天然气化工,1998,27(1):35-38.
- [2] 唐昭峰,等. 国外硫磺回收和尾气处理技术进展综述[J]. 齐鲁石油化工,1997,26(1):58-63.
- [3] 陈赓良. 硫磺回收新工艺——超级克劳斯法[J]. 石油与天然气化工,1990,19(1):10-13.
- [4] 孙玉明. 炼油装置副产酸性气处理技术探讨[J]. 齐鲁石油化工,1999,27(2):122-126.
- [5] 张润立,等. 硫化氢分解制氢气和硫[J]. 石油与天然气化工,1995,24(4):226-230.
- [6] LUINSTRA Ed. Hydrogen form H_2S a review of the leading processes [R]. Process GRI Sulfur Recovery Conference, 7th, 1995:149-165.
- [7] YI Qing-feng, et al. A new approach to the electrochemical decomposition of aqueous hydrogen sulfide solution into sulfur and hydrogen gas [J]. Australian Journal of Chemistry, 2000,53(7):557-560.
- [8] 张义玲,等. 硫化氢分解制取氢和硫技术的进展[J]. 石油化工环境保护,2000,(2):23-28.

(责任编辑 孙燕华)

(上接第 75 页)

4 结 论

(1) 非协调曲边单元离散法,可用于曲率连续变化的 U 型波纹管及有曲率突变的 C 型波纹管。

(2) 该方法可以计算波纹管的轴对称振型及任意环向波数的非轴对称振型。

(3) 虽然不存在一个最低频率对应的固定环向波数,但波纹管的较低固有频率总是出现在环向谐波为 0 和 1 处,即轴对称振型和低阶非轴对称振型在波纹管动态分析中占绝对优势,高环向谐波和高轴向谐波的作用并不明显。

参考文献:

- [1] 王永岗. 储油罐用波纹管的非线性分析及地震反应研究[D]. 北京:石油大学机电工程学院,2000.
- [2] 谢志诚,付承诵,郑思梁. 有曲率突变的轴对称壳(波纹管)的有限元解[J]. 应用数学和力学,1981,2(1):113

- 130.

- [3] 张进国,张对红,吕英民. 旋转波纹管的固有频率的计算[J]. 管道技术与设备,1998,(3):3-6.
- [4] LI Ting-xin, HU Jian, CEN Han-zhao, et al. Research in the field of axial natural frequency and spring rate behavior of bellows [A]. In: Proc 5th Int Conf on Pres Ves Tech[C]. San Francisco, Calif, 1984. 519-529.
- [5] 朱益民,任文敏,张维. 单层波纹管的轴对称振动[J]. 工程力学,1991,8(1):9-14.
- [6] Standards of the Expansion Joint Manufacturers Association (EJMA) [S]. INC(5th edn.), White Plains, New York,1980.
- [7] 王永岗,吕英民,张进国. 波纹管力学性能研究水平述评[J]. 石油机械,1999,27(12):47-50.
- [8] NOVOZHILOV V V. Foundations of the Nonlinear Theory of Elasticity [M]. Rochester, New York: Graylock Press, Inc, 1953.
- [9] GU YAN R J. Reduction of stiffness and mass matrices [J]. AIAA J, 1965, 3(2):380-391.

(责任编辑:沈玉英)

(2) :73 ~ 75.

On the basis of the thin shells theory of Novozhilov theory, the generalized eigenvalue equations for revolving bellows corresponding to non-axisymmetric nature vibration are established and solved with finite element method. By discretizing the bellows with incompatible curved elements of revolving shells, and expanding all dependent variables into Fourier series in circumferential direction, the eigenvalue being corresponding to arbitrary harmonic wave of U-shaped bellows with continuously changable curvity of meridian is given. The given eigenvalue is also favourable to that of C-shaped bellows with abrupt curvity. The correctness of present result is exemplified, and some practical conclusions are obtained. Although there exists no fixed circumferential harmonic number corresponding to the lowest natural frequency of bellow, the symmetric and lower-order non-axisymmetric modes are in the absolute predominance, while the higher-order modes play an unimportant role in its dynamic analysis.

Key words: bellows; abrupt curvature; non-axisymmetry; eigenvalue; incompatible curved elements of revolving shells

SEPARATING HYDROGEN TECHNOLOGY FROM GAS MIXTURE BY FORMING HYDRATE AND ITS RELATIVE DYNAMICS/ MA Chang-feng, WANG Feng, SUN Chang-yu, et al. Faculty of Chemistry Engineering in the University of Petroleum, China, Beijing 102249/ *Shiyou Daxue Xuebao*, 2002,26(2) :76 ~ 78.

The hydrate gas-separating technology was defined according to the different conditions forming the hydrate from gas with different moleculars. A new method for separating or purifying hydrogen from gas mixture is proposed. A set of hydrate gas-separating devices were set up for this purpose. The mixture of methane and hydrogen, and the mixture of dioxide carbon and hydrogen were selected as gas samples for separating experiment. The results confirm that the hydrate gas-separating technology is feasible for hydrogen separation and purification. The vapor/liquid ratio of feed seriously influences the reaction speed. The calculation of the experimental data using the simplified Englezos-Skovborg model shows that the coefficient parameter k is not a constant, but it is related with some special factors, such as gas content in the feed.

Key words: hydrate; purification; separation; hydrogen; dynamics

EXPERIMENTAL STUDY ON RECOVERY OF SULPHUR AND HYDROGEN FROM THE SULPHURETTED HYDROGEN/ LIU Xiang, LI Fa-yong, CAO Zu-gang, et al. College of Chemistry and Chemical Engineering in the University of Petroleum, China, Dongying 257061/ *Shiyou Daxue Xuebao*, 2002,26(2) :79 ~ 81

The double-reaction system is used to treat the acid gas containing H_2S produced in refinery or oilfield to recover sulphur and hydrogen. The effects of volumetric flow rate of liquid, the concentration of trivalent iron ion, and gas flow rate in liquid phase on the mass transfer rate are studied experimentally. The feasibility and the stabilization of the process are tested in the experiment. The results of site experiment show that the absorbance of H_2S under the optimum operating conditions is over 99.9%.

Key words: sulphuretted hydrogen; hydrogen; sulphur; treatment; sour gas; refinery; double-reaction system

KINETICS OF n -HEXANE ISOMERIZATION ON Ni/H-MORDENITE/ LIU Xue-nuan, ZHA Yu-hui and TENG Bo-tao. College of Chemistry and Chemical Engineering in the University of Petroleum, China, Dongying 257061/ *Shiyou Daxue Xuebao*, 2002,26(2) :82 ~ 85.

The kinetics of n -hexane isomerization on Ni/H-mordenite catalyst was studied under the conditions of 483.15 ~ 523.15 K, 1.0 ~ 3.0 MPa, and H_2/n -hexane volume ratio of 10 ~ 40 in a microreactor-gas chromatograph. The effect of weight space velocity on the reaction rate constant was investigated. The results confirmed that the rate of reaction followed a first-order, and the reaction between n -hexane and i -hexane was reversible. The effect of temperature on the reaction rate constant of over-all isomerization was determined on an Arrhenius' type